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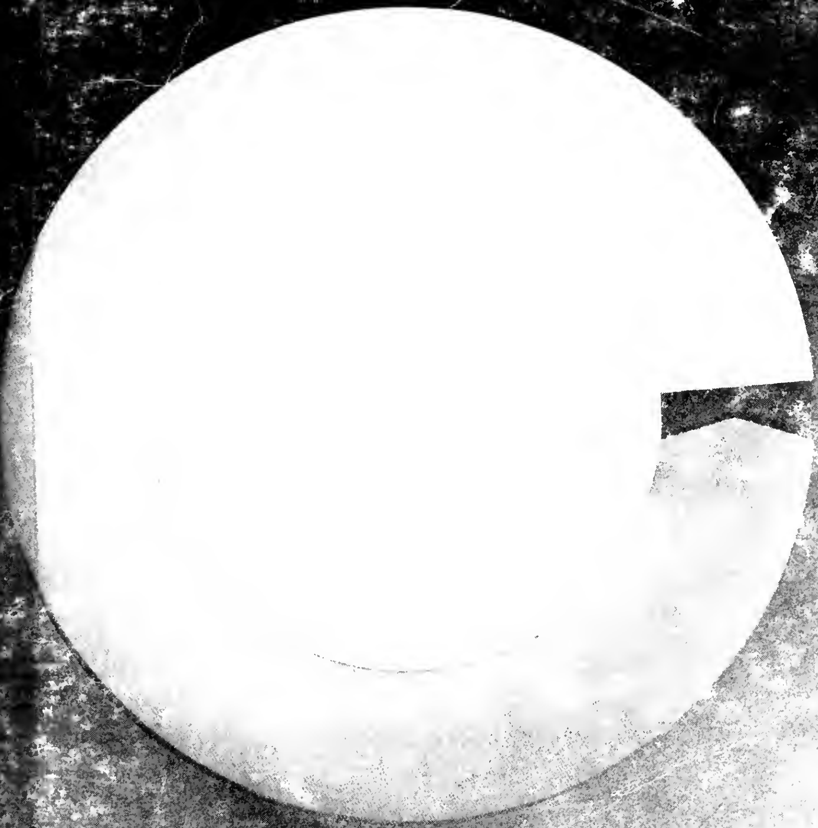
CARBON and the BIOSPHERE



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CARBON and the BIOSPHERE

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Editors

George M. Woodwell
Erene V. Pecan

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PREFACE

The change that man is making in the world carbon budget is among the most abrupt and fundamental changes that the biosphere has experienced in all of world history. The change is in the stuff of life itself and is by now common knowledge. The starkly simple, upward-trending graphs of the CO_2 content of air at Mauna Loa have become a part of the educated man's background in science. But the implications of the change are far less clear than the fact of change. Why has the change not been more? Or less? Where does the carbon go? What does the future hold?

The topic is of unquestioned importance and has been addressed recently by various learned groups (SCEP,* 1970; SMIC,† 1971; and at the Nobel Symposium 20,‡ 1971). These studies have emphasized that prediction is dependent not only on collaboration among scientists of diverse disciplines but on new knowledge: the biosphere is poorly known.

More than a hundred scientists gathered at Brookhaven National Laboratory from May 16 to 18, 1972, under the auspices of the 24th Brookhaven Symposium in Biology to make a new appraisal of the world carbon budget. The appraisal was incomplete. Despite an explicit attempt to include it, there was no treatment of one of the largest and most active pools of carbon: humus and peat. Nonetheless, this publication includes specific attempts at presenting the most modern estimates of various dimensions of the biota, including both biomass and

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***Man's Impact on the Global Environment*, Report of the Study of Critical Environmental Problems (SCEP), The MIT Press, Cambridge, Mass., 1970.

†*Study of Man's Impact on the Climate*, The MIT Press, Cambridge, Mass., 1971.

‡*Changing Chemistry of the Oceans (Nobel Symposium 20)*, David Dryssen and Daniel Jagner (Eds.), Halsteád Press, New York, 1972.

productivity. Many of these estimates are crude, a fact that emphasizes only that the science of the biosphere is still primitive, despite its obvious importance.

The symposium was followed by another meeting of specialists who prepared a summary for The Institute of Ecology. The summary has been reproduced here as an appendix.

Many of our colleagues contributed generously to the meeting and have assisted us in publication. Special thanks go to Virginia Sayre, Jack Craig, Virginia Diebel, Helen Kondratuk, and Irene Rosati of Brookhaven who skillfully tended to the details of the conference. For coordinating and preparing the proceedings of this symposium for publication, we especially thank Anne Goulden, Editorial Branch, Technical Information Center, U. S. Atomic Energy Commission.

George M. Woodwell
Erene V. Pecan
Brookhaven National Laboratory

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THE BIOSPHERE

DANIEL A. LIVINGSTONE
Department of Zoology, Duke University, Durham, North Carolina

When the prospectus of this meeting first appeared, I noted with wry amusement that the symposium on carbon and the biosphere was to consist of two parts—one lecture on the biosphere by my old friend Jack Vallentyne and 19 lectures on carbon by the other participants. I was looking forward with interest to how he would handle this unequal division of responsibility until George Woodwell called to say that discretion had belatedly overcome the usual Vallentyne elan, and that he hoped I would introduce the meeting in Jack's place.

So I spent the last 3 days before the symposium with encyclopedias and textbooks, collecting the conventional wisdom about the biogeochemistry of carbon to see where we stood before the Brookhaven symposium of 1972. The current compendium of settled scientific matters is the McGraw-Hill *Encyclopedia of Science and Technology*, and there I discovered no general agreement even about what the biosphere is. Of two entries for the subject, a brief one is by our missing speaker, Dr. Vallentyne,[1] who defines the biosphere as that part of the earth inhabited by living things and regrets an alternative misguided usage in which "biosphere" refers to the sum total of all plants and animals rather than the place in which they live. The second entry is a three-page account based on just this alternative usage (Mueller).[2]

My own inclination is to follow Vallentyne and regard the biosphere as the place where organisms live rather than the total of all organisms. By either definition the concept of a biosphere embraces two separate ideas: that organisms are important in geochemistry and that the earth is an integrated geochemical system. The first idea was familiar to De Saussure,[3] and the second idea is now standard mental equipment for every reader of *Time* magazine. "Biosphere" is no longer the rallying cry of a small in-group with a private and exciting view of the world. Still, it quite adequately distinguishes the subject of our symposium from other aspects of the study of carbon.

No pools in the carbon cycle seem to be known with satisfactory accuracy. Possible exceptions are the amount of carbon in the atmosphere and the amount dissolved in seawater, but even these are not well enough known for some purposes. For example, it would be highly desirable to have a much wider net of stations measuring the atmospheric carbon dioxide and many more data for the equilibrium carbon dioxide of surface ocean water.

The other major pools are known even less well than the dissolved carbon in atmosphere and ocean. There is no general agreement on the total mass of plants and animals, living or dead. Leafing through a few standard texts and encyclopedias, we find estimates for the size of the biosphere in a non-Vallentynian sense that range from 0.58×10^{18} (Takahashi[4]) to 2.8×10^{18} g (Borchert[5]). Rankama and Sahama[6] give the mass of plants and animals as 20.4×10^{18} g, but that is presumably on a wet-weight basis. To my knowledge, no estimate of the total carbon in groundwater has ever been made. Even data on carbonate equilibrium conditions in groundwater are very scarce (White, Hem, and Waring, 1963[7]). These are large and reactive carbon pools, and it is unsettling that they should be so poorly known.

Technical and geophysical developments of the past decade have drawn attention to interactions between the earth and outer space and to plate tectonics of the sea floor. Both these matters have geochemical implications but are seldom treated explicitly in geochemical budgets. It is comforting to report, on the basis of very crude computations, that the gain of carbon in the form of meteorites seems negligibly small and that loss of carbon from the reactive surface of the earth by sea-floor spreading, although not negligible, is not ruinously large.

The rate of sea-floor spreading seems to be between 1 and 10 cm/year, and the thickness of the sediment on older parts of the sea floor seems to be some 300 m. The total length of the subduction zones is not known. In fact, even the location of subduction zones is established with much less certainty than the spreading that seems to require them. It might not be unreasonable, however, to assume a length of subduction zone for the world of no more than 44,000 km. This is about the length of the Pacific ring of fire which consists in large part of deep-sea trenches which are probably subduction zones and of young mountain belts which may be subduction zones. There is enough length left over to be roughly equal to the combined length of the shorter convergences in other parts of the world. If we assume a mean density of 2.4 for the down-welling rocks and the carbon content of 1% given by Garrels and Mackenzie[8] for modern sediments, we reach an estimate of some 0.003 to 0.03×10^9 tons of carbon being carried down in the zones of crustal convergence. Any substantial entrainment of calcareous sediments would increase the rate considerably but possibly not to so much as 0.3×10^9 tons. This is not a small figure, being about one-tenth as large as the annual combustion of fossil fuels, but it is not so large as to suggest that all classical geochemical computations must be abandoned in the face of sea-floor spreading.

Data for the number of meteorites striking the earth each year are readily available, but data for their total mass are not. If we assume an average mass of a hundred kilograms for 500 meteorites per year, we shall almost certainly be greatly overestimating the total. About 1% of the meteorites are carbonaceous chondrites with up to 5% carbon. The amount of carbon in all other classes of meteorites, including class 2 and class 3 chondrites, is negligibly small in comparison. This leads to the miniscule figure of 25 kg gained each year by this route.

Most of the cosmic material reaching the earth, however, does not fall in the form of meteorites big enough to be collected and counted. It comes as fine dust and has been estimated at from 500,000 to 5,000,000 tons each year (Patterson[9]). Accepting the higher figure and assuming that the proportion of carbon in the dust is similar to that in the meteorites suggest that 2500 tons of carbon might reach the earth each year. Actually, of course, the recognizable dust is only the metallic part. It would not be unreasonable to double the estimate on this account to 5000 tons/year. Even if there are undiscovered errors of as much as two or three orders of magnitude in this computation, the gain of carbon from outer space is too small to be geochemically important. The qualitative carbon chemistry of chondrites is fascinating for the insight it gives us into the chemical history of some astronomical body other than our own planet, but, as a quantitative feature of the carbon cycle on earth, apparently meteorites can be ignored.

During the past few years, some of the most interesting developments in carbon geochemistry have involved the analysis of radiocarbon data in accordance with simple dynamic models of the ocean–atmosphere system. Despite the success of this simple approach, I will enter a plea for attention to some of the more difficult parts of the carbon cycle. In the chain of events from the death of a terrestrial plant through its incorporation in the litter and soil humus, transformation of some of it into the carbonic acid of soil water that is largely responsible for the chemical weathering of rocks, and transfer of the resulting solutions to the sea, there are few simple equilibria and few pools or fluxes that can be measured easily, but these processes are as important as they are difficult to measure.

Measurements of diffusive flux across the sea surface have shown it to be very large, and this largeness occasionally leads to the neglect of other important fluxes in the system. For example, Takahashi,[4] in an otherwise interesting and informative article on carbon dioxide in the sea and atmosphere, says that the carbon dioxide lost from surface ocean water by photosynthesis and biological carbonate precipitation is replaced by diffusive gain from the atmosphere, which is of approximately the same size. He maintains that the contribution from river water is probably on the order of $\frac{1}{500}$ of photosynthetic consumption by marine plants and may be neglected in discussing the source of the carbon removed from the sea biologically.

Takahashi's estimate of total annual photosynthesis at sea is the classic one of Riley, which is now known to have been too high. The gross photosynthesis of the sea is more nearly 50 than 500 times the river input, but there is no reason to expect it to bear any particular relation to any particular input, atmospheric or riverine. The carbon dioxide involved comes mostly from internal recycling, in large part recycling within the surface mixed layer. although there are important inputs by turbulent transfer from the deep water and in places from upwelling as well. There is, in principle, no reason why a marine photosynthetic system should not be completely cyclic with respect to carbon, and no reason at all to believe that the real ocean requires an annual diffusive input equal to the amount of carbon used in photosynthesis.

The diffusive flux from the atmosphere is enormous, but it is offset by an opposing flux of comparable size. Through most of geologic time, the sea has been a source, not a sink, for atmospheric carbon dioxide. The calcium carried down the rivers to the sea has not accumulated there but has been precipitated as carbonate, releasing carbon dioxide equivalent to the carbonate precipitated.

A sudden and massive injection of carbon dioxide into the atmosphere would, of course, reverse the net flow across the sea surface and dissolve oceanic carbonates to establish a new steady state. If all the industrial increase in atmospheric carbon dioxide had occurred in a single year, there is no question that it would reverse the diffusive flow. If the atmospheric carbon dioxide were equilibrating quickly with the enormous mass of oceanic carbon, even the slow addition that has taken place since 1860 would reverse the net diffusive exchange. Actually, however, this is approximately the situation only in the polar oceans. Elsewhere the equilibration takes place initially with only the shallow mixed layer containing a mass of carbon comparable with the mass in the atmosphere. The exchange with deep-ocean water is a very much slower process, so that any increase in the partial pressure of carbon dioxide in the atmosphere will very quickly engender a corresponding increase in back partial pressure from the sea. With the atmospheric carbon dioxide increasing at a rate of 0.5% per annum, we must be very close to the point of reversing the net diffusive exchange across the sea surface. Given the uncertainties in some of the data, we may even have passed it. It is by no means self-evident, however, that the sea has become a net sink of carbon dioxide already, although a progressive slowing down in the rate at which it normally delivers carbon to the atmosphere has been enormously effective in buffering the atmosphere against the effects of industrial combustion, and the enormous diffusive exchange with seawater has been a major control of atmospheric-carbon-isotope geochemistry.

Encyclopedia accounts are biased in the direction of simplicity, and probably the carbon geochemists are really not as enamored of simple quasi-equilibrium models as their accounts for nonspecialists suggest. As an interested and not completely naive observer, however, I would be happy to see more obvious concern with the complex steady-state fluxes through green plants and humus, with carbonic acid in soil water and its reactions with rocks, including igneous ones. Understanding the dynamic response of these parts of the system to atmospheric carbon dioxide content is more difficult than applying Henry's law to the sea surface, but it is likely to be just as important to understanding the behavior of carbon in the biosphere.

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DISCUSSION BY ATTENDEES

Olson: Would not marine photosynthesizers act in the same way as land plants in soaking up excess CO_2 generated by the burning of fossil fuels?

Livingstone: Certainly, but the effect of calcium carbonate precipitation is even more important.

THE ^{14}C CYCLE AND ITS IMPLICATIONS FOR MIXING RATES IN THE OCEAN-ATMOSPHERE SYSTEM

MINZE STUIVER
Departments of Geological Sciences and Zoology, University of Washington,
Seattle, Washington

ABSTRACT

Residence times and exchange rates for carbon in major carbon reservoirs are derived from box-model studies of ^{14}C activity ratios. A diffusion–advection model gives information on oceanic mixing processes and the oceanic transport of carbon of biological origin. This paper summarizes literature associated with this type of "global" study of carbon transfer and storage.

Considerable information on the carbon transfer in nature can be obtained from the differences in the specific activity of ^{14}C in the various reservoirs found on earth. The knowledge of the distribution of the ^{14}C isotope in these reservoirs provides insight into the patterns and rates of large-scale circulation in the oceans as well as in the atmosphere. Box models that describe reservoir properties are used to assess the transfer of radiocarbon between the various reservoirs. Various simplifying assumptions have to be made for a rigorous mathematical treatment of the model. Such studies occasionally give the impression that a precise calculation provides a screen for an imprecise assumption, and the models should be considered a crude approximation only of the gross features of carbon transfer in nature.

In these models the ocean–atmosphere–biota system is divided into a series of independent, well-mixed reservoirs. Carbon dioxide, with a specific ^{14}C activity representative for the reservoir under consideration, is exchanged with adjacent reservoirs. The exchange rates required to maintain a fixed steady-state ^{14}C distribution between the reservoirs are computed.

In this discussion of mean residence times, a reservoir with a steady-state fixed number of molecules, N, and a continuous flux into and out of the reservoir of ϕ molecules per year is considered.[1] The number of particular molecules, n, originally present in the reservoir at $t = 0$ is continuously decreasing with time. The number of these molecules, dn, removed over an interval dt is proportional to the flux and relative concentration n/N of these particular molecules, i.e., $dn = -(n/N)\phi\, dt$. Integration yields $n = Ne^{-\phi t/N}$.

In many instances the transfer process between reservoirs depends on the total amount of material in the reservoirs. Thus in most models the rate of removal depends only on the total number N of the kind of molecule under consideration. The outgoing flux is then given as the product of N and an exchange-rate constant, k. The exchange-rate constant has no clearly defined physical basis but is a useful parameter for box-model studies. With $\phi = kN$, the number of molecules n in the reservoir is decreasing according to $n = Ne^{-kt}$.

The decrease in the number of molecules originally present follows an exponential law similar to radioactive decay, with the decay constant λ equivalent to k. For radioactive decay the average life of an atom is $1/\lambda$ years. In a similar way the average life, or mean residence time, τ, of our particular molecules in the reservoir is $1/k$. The average life τ is, of course, also the time required for the number of original molecules to be reduced to $1/e$ times the number at $t = 0$.

The relation $dn = -kn\, dt$ for a reservoir exchanging with only one other reservoir can be enlarged to $dn = -(k_1 + k_2 + \ldots + k_M)n\, dt$ for a multicomponent system where this reservoir exchanges with M other reservoirs. The average life τ equals, in this instance, $1/(k_1 + k_2 + \ldots + k_M)$; the inverse of this relation yields $1/\tau = (1/\tau_1) + (1/\tau_2) + (\ldots) + (1/\tau_M)$. The equations given here greatly simplify the analysis of box-model systems.

The mean residence time of ^{14}C in a specific reservoir is not identical to the stable-carbon residence time. Because of radioactivity, the removal rate includes both the physical removal to other reservoirs and the ^{14}C decay rate, $-\lambda N$. Mean residence times of the ^{14}C molecules may also differ slightly from the stable species because of isotope fractionation in the removal processes. The small isotope-fractionation effects depend on isotopic-mass differences only and can occasionally be neglected in the calculations.

The development of box models of increasing complexity has resulted in an understanding of the mean residence times of carbon in the atmosphere and in the various regions of the sea and has also provided information on the exchange rate between atmosphere and sea. It is easy to get lost in the mathematical details and nomenclature of these box models. We can become familiar with the general procedures by discussing here the calculation of the residence time of carbon dioxide in a simple box model involving the atmosphere and the mixed layer of the oceans. For the more complicated models, only the results are given; the technical details can be found in the original publications.

In a steady-state condition, the net transfer of ^{14}C to the oceans equals the total ^{14}C decay in the large oceanic reservoirs. If one assumes that the exchange of carbon is uniform over the oceans, the following equation holds:

$$\phi_{a-m}\, C_a A = \phi_{m-a}\, C_m A + \lambda C_0 N_0$$

where ϕ_{a-m}, ϕ_{m-a} = exchange rates of CO_2 (moles m^{-2} year^{-1}) through the interface of atmosphere and surface of the mixed layer of the oceans

C_a, C_m, C_0 = ^{14}C activities,[2] respectively, of atmospheric CO_2, surface ocean CO_2, and average ocean CO_2 (moles $^{14}CO_2$/mole CO_2)

A = area of ocean–atmosphere interface (m^2)

λ = ^{14}C decay constant

N_0 = total amount of CO_2 in the oceans (moles)

The rate of loss of CO_2 to the sediments and the influx of bicarbonates from rivers are negligible; thus the exchange rate from atmosphere to oceans equals the rate from oceans to atmosphere for a steady state. Substituting $\phi_{m-a} = \phi_{a-m}$, one arrives at

$$\phi_{a-m} = \frac{\lambda (C_0/C_a) N_0}{[1 - (C_m/C_a)]\, A}$$

The knowledge of the ratio of the specific ^{14}C activities in average ocean water, mixed layer of the oceans, and the atmosphere leads directly to a value for an average exchange rate. Broecker[2] estimates C_0/C_a as 0.85 ± 0.05 and C_m/C_a as 0.95 ± 0.015. These values yield a rate of 20 ± 7 moles m^{-2} year^{-1}. With, on the average, 100 moles CO_2/m^2 in the atmosphere, which is equivalent to 140 moles CO_2/m^2 of oceanic surface, the mean residence time for atmospheric CO_2 is 7 years.

For the above-mentioned calculation, the CO_2 exchange between oceans and atmosphere has to be uniform on a global scale. This seems unlikely because wind velocity influences the rate of exchange. Kanwisher[3] measured the rate of gas exchange across the air–seawater interface and found a rate of exchange approximately proportional to the square of the wind speed. Wind velocities are, on the average, considerably higher in the Antarctic region than in the rest of the world, and the CO_2 exchange rate in the Antarctic will be several times higher than in the rest of the oceans. This would lead to an increase in residence time for CO_2 in the atmosphere because the Antarctic Ocean has a ^{14}C to ^{12}C ratio about 8% lower than the remaining mixed layer of the oceans. A residence time of about 10 years seems to be an upper limit.[2]

Residence times for atmospheric CO_2 can also be obtained from the rate of uptake of bomb $^{14}CO_2$ in the oceans. For instance, between 1963 and 1965 the atmospheric excess ^{14}C inventory decreased at a rate equivalent to a half-life of 3.3 years, which gives an upper limit of 4.8 years for the mean residence time of a ^{14}C atom in the atmosphere.[4] About 18% of the $^{14}CO_2$ leaving the atmosphere goes into the biota,[1] giving an upper limit of 5.8 years for the mean residence time of atmospheric CO_2 before uptake by the oceans. This estimate is an upper limit only, because during the 1963 to 1965 period much of the excess ^{14}C was stored in the stratosphere and unavailable for transfer to the oceans. By taking into account the dependence of the CO_2 exchange on wind velocity, Young and Fairhall[4] also developed a model giving mean tropospheric residence times as a function of latitude. They conclude that the bulk of excess ^{14}C produced by past nuclear explosions will eventually be taken up by the oceans of the Southern Hemisphere.

As discussed earlier, exchange rates between troposphere and the mixed layer of the oceans can be derived from (a) the transfer of excess bomb ^{14}C to the oceans and from (b) steady-state equilibrium between natural ^{14}C exchange over the ocean—air interface and ^{14}C decay in the oceans. In addition, exchange-rate constants can be calculated from (c) the change in atmospheric ^{14}C activity caused by dilution of the atmospheric reservoir through addition of industrial CO_2 and (d) the natural ^{14}C balance in the atmosphere where natural production of ^{14}C balances the decay in the atmosphere and the net transfer to the oceans. The results obtained from atomic-bomb radiocarbon transfer between atmosphere and oceans include atmospheric CO_2 residence times of 4, 5.4, 25, 4, and 5 to 10 years reported, respectively, by Lal and Rama,[5] Münnich and Roether,[6] Bien and Suess,[7] Young and Fairhall,[4] and Nydall.[8] From radiocarbon decay in the oceans (method b) Broecker[2] gives a residence time of 7 to 10 years, whereas Craig[1] arrives at a 4- to 10-year value from ^{14}C-production-rate considerations (d, above). Fergusson[9] and Revelle and Suess[10] calculate, from the change in specific ^{14}C activity caused by industrial CO_2, residence times of, respectively, 2 to 7 years and about 10 years.

The 25-year value was calculated on the basis of major uptake of excess bomb ^{14}C by the biosphere. The other workers suggest a smaller biospheric contribution, and a 5- to 6-year atmospheric residence time for CO_2 transfer between troposphere and the oceans seems a reasonable meeting ground.

The complexity of ocean-water circulation makes the application of box models to the investigation of mixing rates and patterns in the oceans more difficult. It would be possible to explain the isotope distributions with a large variety of models. However, only when the isotope results are tied to other oceanographic data is it possible to obtain suitable models.

Oceanic mixing itself involves complicated contributions of both advection (or convection) and diffusion. Advective processes involve regular patterns of water movement, whereas in diffusive processes irregular movements of water called turbulence, together with molecular diffusion, provide exchange without net transport of water. Advective processes are normally large-scale events, whereas diffusive processes are restricted to much smaller dimensions.

For the box-model studies, the properties of water in each box are averaged, and one attempts to see changes only as between boxes. Both horizontal and vertical exchange have been studied. Some of these models are given in Fig. 1. In the terminology of Broecker,[2] the models are classified as: (1) the two-layer

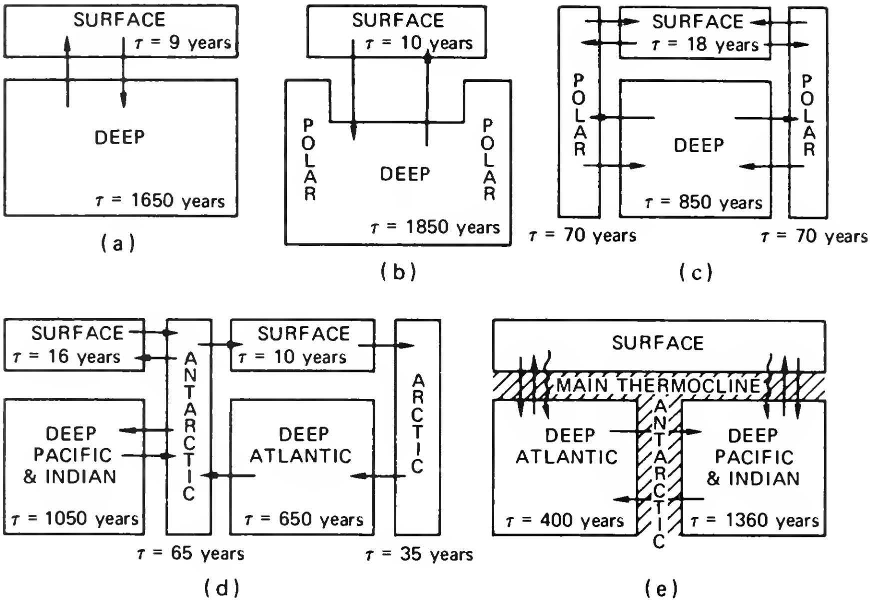

Fig. 1 Some examples of oceanic circulation box models. The directions of exchange are shown by solid arrows; wavy lines give particulate transport. The calculated residence times, τ, are inside each reservoir. The relative dimensions of the boxes are not identical with the actual ratios of reservoir sizes. Ocean–atmosphere exchange has been omitted. (a) Two-layer model.[1,11] (b) Outcrop model.[12] (c) Three-reservoir model.[13] (d) World-ocean model.[13] (e) Simplified mixing cross model.[14]

model,[1,11] (2) the outcrop model,[12] (3) the three-reservoir model,[13] (4) the world-ocean model,[13] and (5) the mixing cross model.[14] All models incorporate a well-mixed surface-layer reservoir and a much larger deep-ocean reservoir. The oceanic deep-water masses are fed by waters sinking in the polar regions; this has been taken into account (1) in the outcrop model by having the deep water reaching the surface over a portion of the oceans, (2) in the three-reservoir and mixing cross model through a well-mixed reservoir at the end of the oceans, and (3) in the world-ocean model through two reservoirs of vertical mixing (Arctic and Antarctic). For each model, the mixed-surface-layer depth is taken as 100 m; the calculated residence times are given in the figure. Mixing is assumed to take place only as indicated by the arrows; for instance, in the world model [Fig. 1(d)] a cyclic flow is postulated for the Atlantic and no direct mixing between the surface and deep reservoirs.

A comparison of the box models with the much more complicated water-mass structure of the oceans clearly indicates a large degree of oversimplification. The overall features of the models, however, lead to some important general conclusions. For instance, residence times for the Pacific and

Atlantic deep water are, respectively, about 1000 and 600 years. These numbers are approximate only as the exact time is strongly dependent on the CO_2 exchange rate through the polar seas.

It should be noted that not all information in the models is derived from ^{14}C data. In the simplified mixing cross model, we can evaluate the rate of exchange between the three major water types in the ocean (surface water, North Atlantic deep water, and Pacific and Indian deep water) by determining the eight unknown fluxes from material-balance considerations for H_2O, ^{14}C, and total CO_2 and from the requirement that the ^{18}O–salinity relations observed in the ocean are not to be violated.[14] This model also takes into account the particulate transport of carbon to the deep-ocean reservoirs. The organic material and calcium carbonate produced in surface waters by organisms sink under the influence of gravity and introduce a carbon transport that is not exclusively associated with water movement. Thus the unknowns in the simplified mixing cross model involve six water-related fluxes and two fluxes of carbon-bearing particles from the surface ocean into the deep reservoirs.

Most of the particles transported downward are redissolved or oxidized in the deep ocean. Of the particulate carbon,[15] about 80% is in the form of organic debris and 20% is in the form of $CaCO_3$. Whereas the organic debris is depleted in ^{13}C by about 2% relative to the dissolved carbon in surface water,[16] the $CaCO_3$ shows negligible isotope separation. Because the ^{14}C fractionation amounts to twice the ^{13}C fractionation, the composite particulate carbon flux is about 3% depleted in ^{14}C relative to surface waters.

The mixing-cross-model calculations give a best estimate of the flux of $CaCO_3$ necessary to provide the carbon to the deep waters of 3.2 g cm^{-2} 1000 years^{-1} in the Atlantic and 1.4 g cm^{-2} 1000 years^{-1} in the Pacific. Actual measured rates in limited oceanic areas indicate calcite accumulation rates of about one-half of these values.[14] Although agreement between predicted and actual values is only within a factor of 2, it still provides support for the magnitude of oceanic overturn time predicted by the mixing cross model.

Since most models are concerned with steady-state conditions, it is essential to use ^{14}C data that were obtained before appreciable quantities of bomb ^{14}C were added to the surface waters. Prebomb measurements available are those of Broecker[2] for the Atlantic and of Bien, Rakestraw, and Suess[17] for the Pacific and Indian oceans. These data are given in Figs. 2 and 3.

The ^{14}C deficiency of the oldest ocean waters is about 10% for the Atlantic, 10% for the Antarctic, and 25% for the Pacific Ocean (after correction for isotope fractionation). This would lead to apparent ^{14}C ages of 800 years for the Atlantic and Antarctic oceans and 2000 years for the Pacific Ocean. The apparent-age values are only crudely related to the residence time in those reservoirs. For example, one of the reasons for the old age of the deep-seated Pacific waters is the addition of Antarctic waters with an apparent age of about 800 years. Only a proper evaluation of box models, using specific ^{14}C activity data, leads to useful residence times for the various reservoirs.

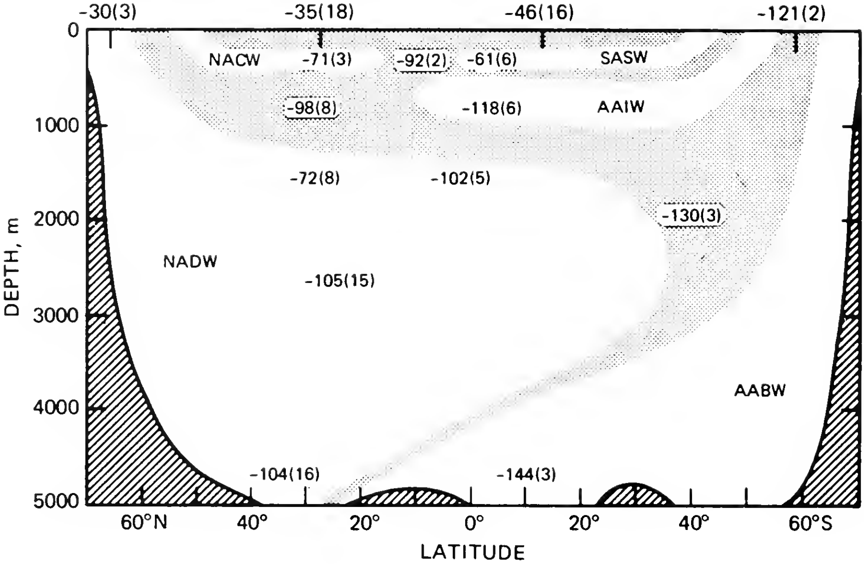

Fig. 2 Average ^{14}C specific activities of bicarbonate in the Atlantic Ocean, as given by Broecker.[2] The number of samples measured is given in parentheses; the other values give the per mille ^{14}C deviation from the Lamont standard. Water masses are given by NACW (North Atlantic Central); SASW (South Atlantic Surface); AAIW (Antarctic Intermediate); NADW (North Atlantic Deep); and AABW (Antarctic Bottom).

The preceding data depict a general northward and southward movement, of, respectively, the bottom Pacific and Atlantic ocean waters. Bien and coworkers[17] estimate from the change in specific ^{14}C activities an overall northward velocity of 0.6 to 0.7 mm/sec for the deep Pacific waters.

The complications introduced by particulate transport to the deep ocean are neglected in many box-model studies. However, for a simple two-box model, Lal[18] has shown that the calculations of residence times are not affected by particulate transport, since the ratio of the specific activities turns out to be independent of the particulate flux. Its effect is to reduce the concentration of both ^{14}C and CO_2 in the mixed layer, affecting both to the same extent.

Particulate (or "biotic") transport is of importance for differences in both the specific ^{14}C activity and the total CO_2 concentration between surface and deep waters. A typical profile[19] in the Pacific at 28°29′N, 121°38′W is given in Fig. 4. The depletion of total CO_2 in the surface waters and the CO_2 maximum at a depth of about 1 to 2 km are attributed to biotic transport.

In a two-reservoir model, the net input of ^{14}C in the deep reservoir is equal to $\lambda C_d N_d$ (where C_d = specific ^{14}C activity and N_d = total number of CO_2 molecules in the deep-ocean reservoir). This net input is provided by the particulate carbon dissolved in the deep ocean and by the net flux of CO_2 over

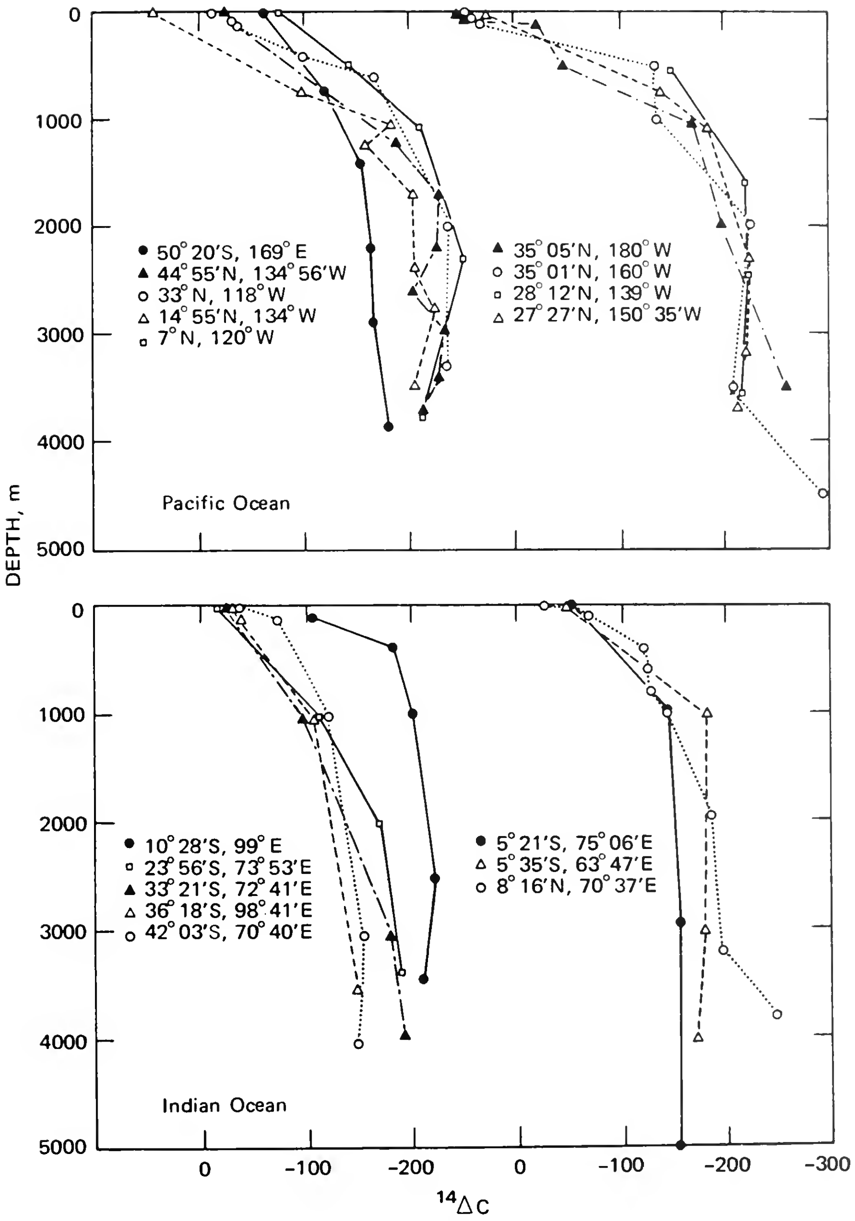

Fig. 3 The ^{14}C specific activities of ocean-water bicarbonate as a function of depth for the Pacific and Indian oceans as given by Bien, Rakestraw, and Suess.[17] Δ^{14}C is the per mille deviation from 19th century wood after correction for isotope fractionation.

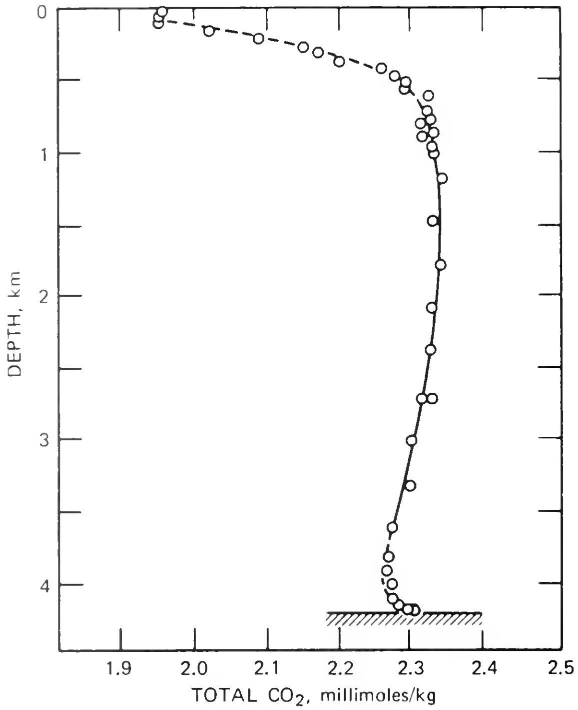

Fig. 4 Total CO_2 content as a function of depth in the Pacific Ocean at 28°29′N, 121°38′W. The solid curve was calculated for a B/w value of 0.047, with B constant. From Craig and Weiss.[19]

the boundary between the mixed layer and deep ocean. The net ^{14}C flux between the deep-water and mixed-layer reservoirs through the standard advection–diffusion exchange appears, surprisingly, to be about zero[20] or even directed upward.[18] Although the specific ^{14}C activities are highest in the mixed surface layer, the increase in total CO_2 for the deeper waters results in a total amount of ^{14}C transported from the deep reservoir to the mixed layer at least equal to the amount transported downward (biotic transport not included). The transport of particulate carbon to the deep waters would then provide almost entirely for radioactive-decay losses in these waters.

Since the gradients in specific CO_2 concentration are often large compared to the gradients in specific ^{14}C activity, the use of specific ^{14}C concentrations (^{14}C atoms per cubic centimeter) gives a better approximation of reality for box-model calculations[18] than the traditionally used specific ^{14}C activity (^{14}C/carbon). These effects have been taken into account in a diffusion–advection model with particulate flux, recently discussed by Craig.[20] With the use of Craig's description, this model is outlined in the following paragraphs.

For the circulation models in use in oceanography, the steady-state vertical profiles of dissolved components are calculated by fixing two boundaries. In its one-dimensional form, the theory is only concerned with vertical distribution, and interior horizontal flow is not important. The basic equations take into account the changes in water density as a function of depth. For a component with specific concentration C, the change in concentration with time t is given[21] by

$$\frac{\partial C}{\partial t} = K \frac{\partial^2 C}{\partial z^2} + \frac{1}{\rho}\frac{\partial}{\partial z}(\rho K)\frac{\partial C}{\partial z} - w\frac{\partial C}{\partial z} - \lambda C + B$$

where K = vertical diffusion coefficient
ρ = density
w = vertical advection velocity
λ = decay constant
B = biotic production rate

For a stationary profile the change in concentration with time equals zero; in addition, the product of density and advection velocity has to be constant for a steady-state water-mass transport. With ρw constant and if we assume that the mixing parameter K/w is independent of depth, it is clear that $(\partial/\partial z)(\rho K) = 0$, and the preceding equation becomes

$$K\frac{\partial^2 C}{\partial z^2} + B = w\frac{\partial C}{\partial z} + \lambda C \qquad (1)$$

This second-order differential equation provides a general solution for C between two boundaries, $z = 0$ and $z = z_m$, with z_m the mixing interval. These boundaries are normally taken in such a manner that they coincide with marked inflection points associated with water-mass boundaries. For our model the boundaries coincide for the Pacific with the obvious geographical limitations of the ocean floor and with (1) the boundary between thermocline layer and deep water at 1 km depth and (2) the boundary between deep water and bottom water at 4 km depth.

Both the temperature and the salinity of ocean waters are conservative properties (only influenced by mixing, $B = 0$) and nonradioactive ($\lambda = 0$). For these components the solution to Eq. 1 becomes $C - C_0 = (C_m - C_0)\, f(z, z_m, K/w)$. Thus, when salinity is plotted as a function of potential temperature, a linear relation should result because for their ratio the function f cancels. Such a linear relation is found for the 1- to 4-km-deep Pacific water, confirming the applicability of the model over this region. The deep Atlantic is more complicated with regard to this aspect since at least two or three such regions can be identified.

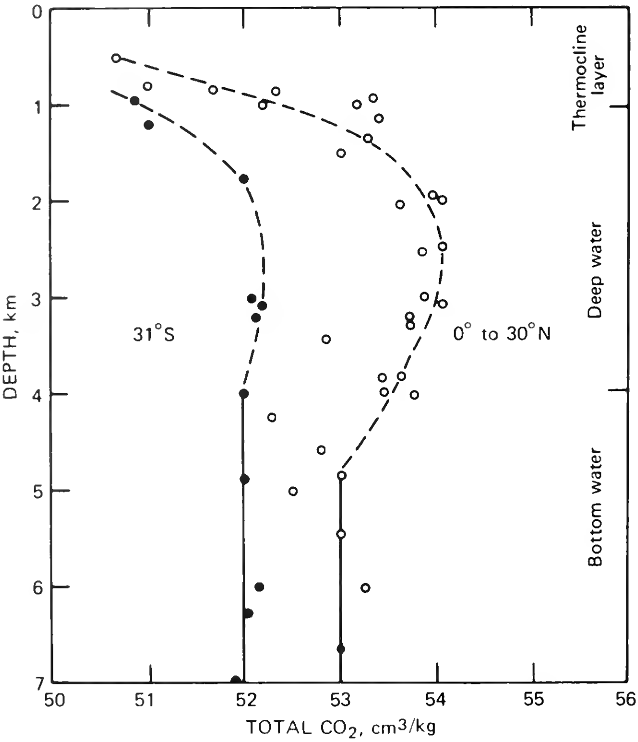

Fig. 5 Total CO_2 profiles in the Pacific at 31°S as given by Weiss and Craig[27] and at 0 to 30°N as given by Li, Takahashi, and Broecker.[15]

The thermocline layer normally shows a much more complicated picture owing to subsurface currents with advective cores and cannot be treated in a simple theoretical manner.

The bottom-water layer contains the more or less horizontal flow of renewal water from the polar regions and is assumed to form a uniform layer below 4 km depth.

The function f, and consequently the mixing parameter K/w, can be determined from both temperature and salinity profiles. An average value of 1 km is representative for this parameter in the deeper Pacific. The positive value of K/w implies upward advection needed to balance downward heat diffusion from the surface and to account for bottom water formed by sinking at polar latitudes.

Equation 1 also can be applied to the total CO_2 profile in the Pacific (Fig. 5). The dashed line in Fig. 5 represents Craig's best possible fit of the solution of Eq. 1 to the available data ($B \neq 0$, $\lambda = 0$). The values of B/w for the best possible fit are 0.60 (cm^3/kg)/km for the 31°S data, and 0.85 (cm^3/kg)/km for the 0 to 30°N data.

As discussed previously, the mixing-cross-model studies indicate a $CaCO_3$ production rate of 1.4 g cm^{-2} 1000 years^{-1} for the Pacific Ocean. The total carbon flux, including organic carbon, is five times larger and would be equivalent to $B = 5 \times 10^{-3}$ cm^3 CO_2 produced annually in 1 liter of water for an average water column of 3500 m length. This value, when combined with the B/w value derived from the preceding total CO_2 data, yields a vertical advection velocity, w, of 4 m/year. With a value of 1 km for the mixing parameter, the corresponding value for the eddy-diffusion coefficient K is 1.3 cm^2/sec.

The values obtained for K, w, and B in the preceding manner can be applied to Eq. 1 describing the ^{14}C concentration in the deeper Pacific waters. (See Craig[20] for more detailed discussion.) The particulate flux produces a ^{14}C flux equal to the product of the particulate flux and the specific ^{14}C activity of the material transported downward. Isotope fractionation causes, as discussed, a 3% depletion in ^{14}C of B relative to surface ocean water, whereas the ocean surface waters are depleted by about 4% in ^{14}C when compared with the modern ^{14}C oxalic acid standard.

The actual profiles of the absolute ^{14}C concentration for the few available data in the deeper waters appear nearly constant in the deep Pacific, with a random scattering of about ±1.5%. When the general solution of Eq. 1 is applied to the data, a best fit is obtained for w = 5 m/year. However, the scattering of the measured points is relatively large; as a result, any value of w in the range of 2 to 20 m/year fits the data.

The near constancy of ^{14}C concentrations in the deeper Pacific and the nearly similar value of ^{14}C concentrations in the thermocline layer indicate, as already mentioned, a lack of net transport of ^{14}C through advection and diffusion between those reservoirs.

Essentially Eq. 1 is simplified to $C^* =$ constant and $B^* = \lambda C^*$ ($C^* = {}^{14}$C concentrations). The biotic production rate B can be calculated from this relation and also w through the B/w ratio obtained from total CO_2 profiles.

A more detailed analysis of the ^{14}C concentration profiles will only be possible when both specific ^{14}C activities and total CO_2 concentrations become available with a precision of 0.5% or better. Until then the ^{14}C profiles contribute in the advection–diffusion model only limited knowledge to the parameters associated with mixing processes in different parts of the Pacific Ocean.

The bottom waters in the oceans contain the horizontal water flux that provides the vertical advection flow in the one-dimensional advection–diffusion model. As mentioned, the reduction in specific ^{14}C activity of 3- to 4-km-deep water, when moving from the South to the North Pacific, indicates northward velocities of about 0.6 mm/sec, according to Bien and coworkers.[17] This calculation is valid when the bottom waters can be considered a closed system, with the only changes in ^{14}C activity provided by radioactive decay and by addition of CO_2 from oxidation of organic material in situ. In the advection–

diffusion model with particulate flux, however, total ^{14}C concentrations have to be taken into account. The reduction in specific ^{14}C activity in the deep Pacific along the South–North traverse is accompanied by an increase in CO_2 content, and the resulting total ^{14}C concentration is practically identical in these areas.[20] Since the vertical gradient of the ^{14}C concentration is zero, the net addition of ^{14}C through diffusion and advection to the bottom waters is zero. In addition, the change in total ^{14}C concentration, when traveling from South to North, is also zero. As a result, it is concluded that the ^{14}C flux provided by biotic transport to the bottom waters during its travel time is equal to the loss of ^{14}C through decay over the same interval. The change in specific activity during travel from South to North is then mainly caused by diffusive CO_2 from higher levels into the bottom waters. This results in an increase in total CO_2 but a lower specific activity because specific ^{14}C activities are slightly lower at higher levels.[21] The model implies shorter horizontal travel times and larger flow velocities, as the reduction in specific activity is only partially due to in situ decay.

Water-circulation patterns at abyssal depths provide additional complications for horizontal-flow-velocity calculations. Only the western boundary current would provide a straight South–North trajectory over the equator for the deeper portions of the Pacific.

The advection–diffusion model is only valid if oxidation of organic material from the particulate flux actually occurs in the deep ocean. Suess and Goldberg[22] cite two studies[23,24] which show that this premise has to be examined in more detail. The arguments involve (1) a correlation between salinity and dissolved oxygen, indicating a lack of measurable effects of respiration on the concentration of dissolved oxygen; and (2) the lack of variability in the concentration of dissolved organic carbon in deep water which would indicate that this material is highly resistant to oxidation. The conclusion of Menzel and Ryther[23] is that the entire biochemical cycle of organic matter appears to occur in the upper 300 m of the ocean. Craig,[25,26] on the other hand, discusses extensively the above-mentioned arguments and concludes that in situ oxidation and solution of carbon in the Pacific occur at sufficient rates for the applicability of the advection–diffusion model with particulate transport. His main argument is the consistency of the calculated results with the profiles obtained in the deep water for total CO_2, ^{14}C, ^{13}C, O_2, and alkalinity.

The controversy involving the biotic component for ^{14}C transport in the deep oceans has to be resolved before more refined interpretations of the ^{14}C distributions can be made. In one of the more recent articles,[27] it is concluded that, until a large number of detailed profiles on total CO_2, ^{14}C, ^{13}C, alkalinity, and O_2 are accumulated, all interpretations of the present library of data should be regarded as highly tentative and probably incorrect. Perhaps this conclusion should be taken more seriously.

ACKNOWLEDGMENT

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DISCUSSION BY ATTENDEES

Botkin: Two students at Yale, along with other workers in the United States, have found that soil bacteria and fungi are a sink for CO.

PREDICTION OF CO_2 IN THE ATMOSPHERE

LESTER MACHTA
Air Resources Laboratories, National Oceanic and Atmospheric Administration,
Silver Spring, Maryland

ABSTRACT

Predictions of future and past carbon dioxide concentrations have been derived from a simple multireservoir exchange model: stratosphere, troposphere; mixed layer of the ocean, deep ocean; short-term land biosphere, long-term land biosphere, and marine biosphere. All exchanges are prescribed from literature or personal estimates except the troposphere–mixed ocean layer that is obtained from a trial-and-error procedure using bomb $^{14}CO_2$ as a tracer. On the basis of reasonable estimates of growth in the use of fossil fuel, the atmospheric CO_2 content predicted for the year 2000 is about 385 ppM, compared to about 320 ppM observed at present. The uncertainties in the model are probably less significant using the above-mentioned procedure than the assumption that the oceans and biosphere will continue to behave in the future as in the 1960s. The so-called greenhouse effect, using a simplified one-dimensional (vertical) model of the atmosphere, calls for about a 0.5°C warming from the increase of CO_2 to 385 ppM. But this estimate of 0.5°C is on even shakier grounds than the forecast of future CO_2 concentrations.

This paper is offered from the viewpoint of a meteorologist concerned with predicting the possible future climatic change due to the increase of carbon dioxide in the atmosphere. There are two aspects of this climatic prediction. First, the fate of the added CO_2 in future years and second, the possible climatic change from atmospheric increases. We shall primarily discuss the first of these topics and touch only lightly on the second. Future CO_2 in the air depends on two factors: first, the added fossil-fuel carbon dioxide injected into the air and, second, the apportioning of this carbon dioxide between the atmosphere and the reservoirs with which it can exchange.

Dr. Ekdahl, in his paper, discusses in much greater detail the observed data for the growth of carbon dioxide in the atmosphere at Mauna Loa and the South Pole. Other data, such as those collected by Bischof[1] in Sweden and by the National Oceanic and Atmospheric Administration aboard Ocean Weather Ship

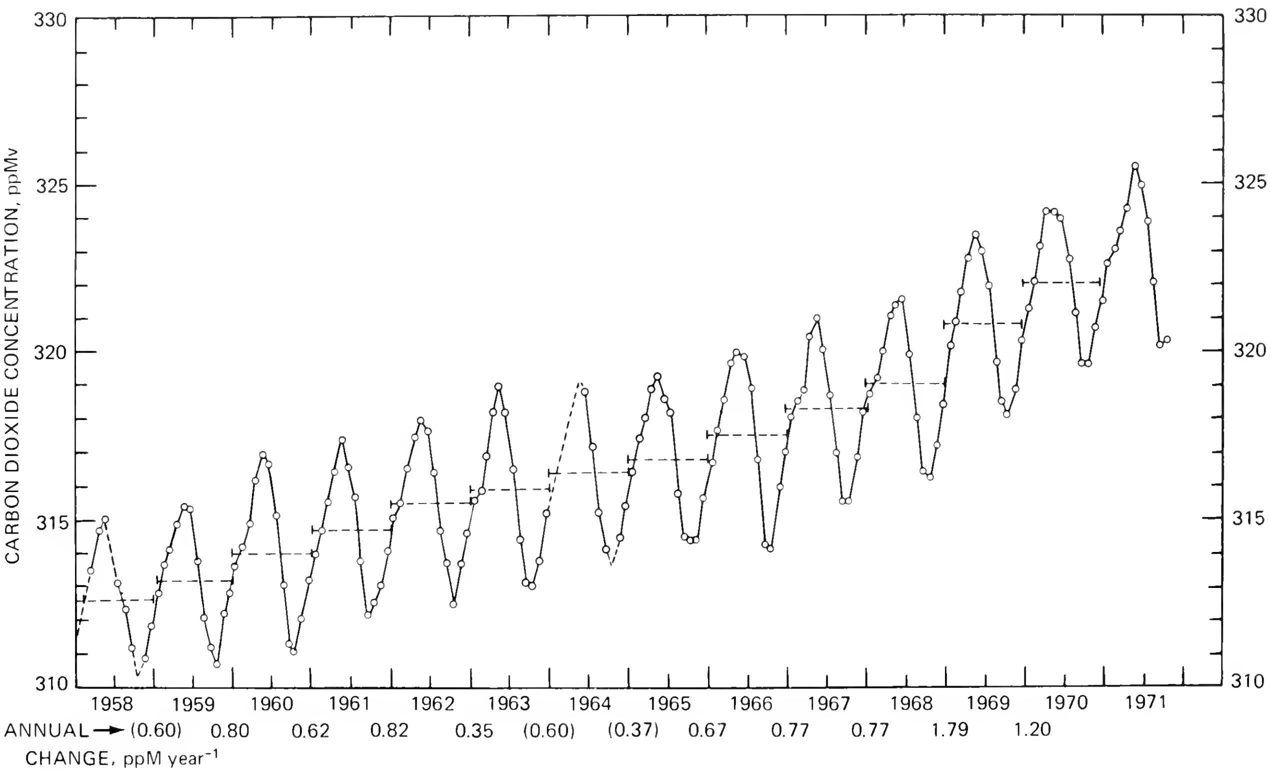

Fig. 1 Mean monthly CO_2 concentrations at Mauna Loa. Horizontal dashed lines indicate average yearly value. Annual changes, in parentheses, are based on incomplete record. (Sources of data, Pales and Keeling[9] and Keeling and Bainbridge.[10])

Charlie and in the western United States,[2] support the trends on Fig. 1, the mean monthly carbon dioxide concentrations at Mauna Loa. There are two very obvious features in this figure. The first is a long-term increase and the second a strong seasonal variation. It is the long-term increase projected into the future that will be discussed. Between the period 1958 and 1971, the growth of CO_2 in the air is about one-half that put into the air by the fossil-fuel CO_2 if it is uniformly distributed throughout the atmosphere. The other half has gone into the biosphere or into the oceans. The prediction of this partitioning into the other reservoirs is needed to forecast future CO_2 concentrations.

THE MODEL

Figure 2 shows the model used. It contains a troposphere, a stratosphere, a mixed layer and a deep layer of the ocean, a long-term biosphere, a short-term biosphere, and a marine biosphere. The exchange between atmosphere and ocean is based on first-order kinetics, whereas the uptake of carbon by each biosphere is the net primary production (NPP). I am indebted to Jerry Olson (Oak Ridge National Laboratory) and George Woodwell (Brookhaven National Laboratory) for most of the details of the biosphere, but I, rather than they, must take the blame for any of the inaccuracies. The exchange between stratosphere and troposphere is based on the fact that radioactive material in the stratosphere has a residence time of about 2 years. The exchange between the deep and mixed layers of the ocean is based on the fact that the average age of the carbon in the deep ocean is about 1600 years. The values for the NPP are taken either from the estimates that were given to me by Woodwell and Olson or from Lieth.[3] The last and most important exchange is that between the atmosphere and the mixed layer of the ocean which is based on the $^{14}CO_2$ from nuclear tests.

Figure 3 shows the time history of ^{14}C atoms produced by nuclear tests in the troposphere and in the entire atmosphere to about 30 km as derived from data collected by the U. S. Atomic Energy Commission mainly over North and South America. The sharp increases of these curves reflect periods with active testing. After about 1963 there were only a few injections into the atmosphere, and small corrections have been made for these.

After about 1963 the $^{14}CO_2$ content of the entire atmosphere decreased. This fact implies that there has been a transfer to other reservoirs, into either the ocean or the biosphere. We have specified the transfer into the biosphere; hence the remaining atmospheric decrease must be the result of CO_2 entering the oceans. This reasoning and Fig. 2 form the basis for the exchange coefficient between the atmosphere and the ocean, using a trial and error procedure. The mean residence time in the atmosphere for a CO_2 molecule becomes about 5 years. The trial and error procedure also provides a mean residence time of carbon and the carbon content of the mixed layer of the ocean. This carbon content corresponds to the depth of the mixed layer of 110 m. It represents the

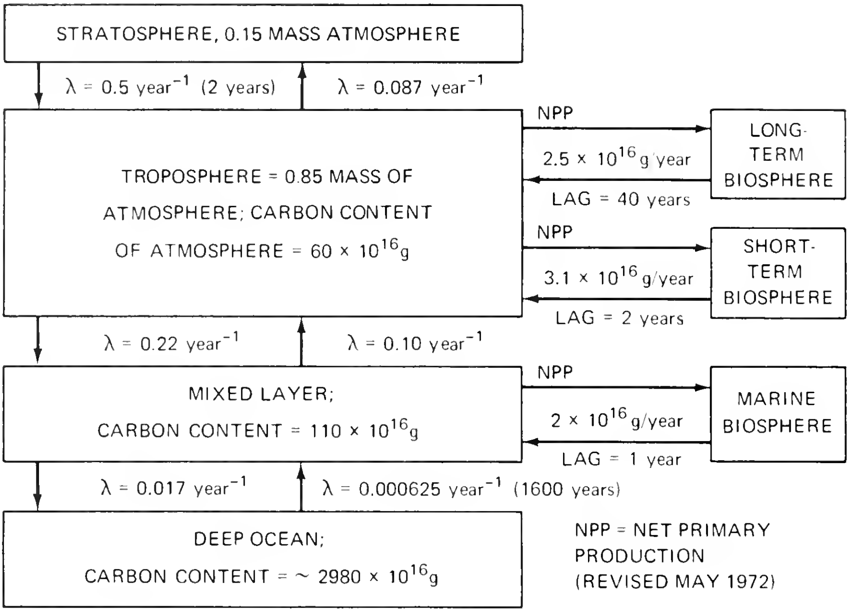

Fig. 2 The model of the three reservoirs of CO_2. The quantity λ denotes the fraction of the CO_2 in one reservoir being transferred to an adjacent reservoir according to the sense of the arrow.

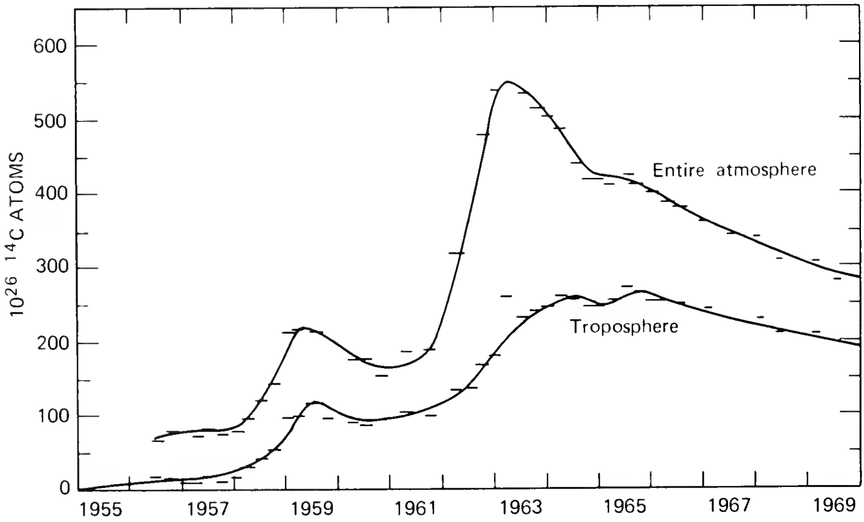

Fig. 3 The time history of ^{14}C atoms produced by nuclear tests in the troposphere and in the whole atmosphere (up to 30 km). (Source of data, Telegadas.[11])

global average depth into which relatively rapid mixing of CO_2 occurs. The 5-year atmospheric residence and 110-m mixed-layer depth represent significant changes from the original model[4] and are due to programming errors.

The amount of fossil-fuel CO_2 expressed in grams of carbon[5] that have been added to the atmosphere until the last United Nations report in 1968 has been followed by an annual growth rate of 4% per year between 1969 and 1979 and a 3½% annual growth rate between 1980 and 1999. When this fossil-fuel CO_2 is added to the atmosphere via the model, we obtain a prediction of the changes in CO_2 content from 1860 to 2000. This prediction appears in Fig. 4, using the

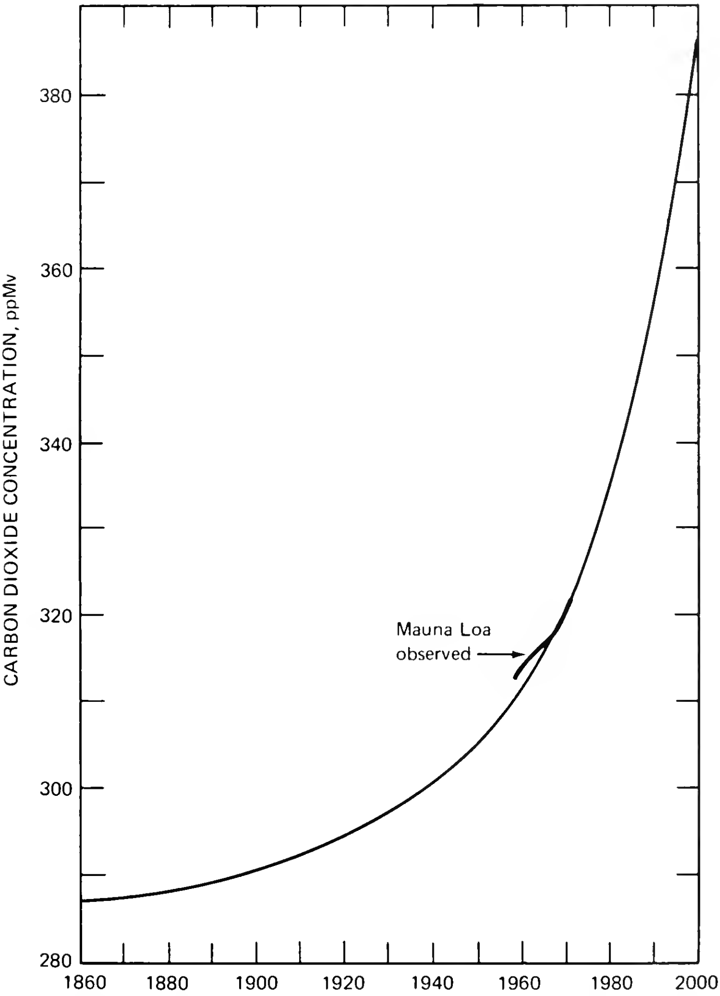

Fig. 4 The predicted time history of global atmospheric CO_2 from 1860 to 2000.

Mauna Loa concentration of about 322 ppM in 1970 as the base. The concentration of CO_2 will be about 385 ppM in the year 2000 and was about 290 ppM at the beginning of the industrial area. This latter value is approximately the correct order when compared to the poorly measured data in the latter part of the 19th century.

The partitioning of fossil-fuel CO_2 molecules among the three reservoirs shows that, as of 1970, about 65% of the fossil-fuel CO_2 remained airborne; half of the remainder appears in the oceans, mostly in the mixed layer, and the other half in the biosphere, almost entirely in the long-term land biosphere. This model assigns a surprisingly large fraction of the fossil-fuel CO_2 to the biosphere relative to the oceans. During the period 1958 to 1970, the average airborne fraction of the fossil-fuel CO_2 was between 60 and 65%, which is about 10% more than is suggested by the Mauna Loa and other stations.

The following are some of the special details of the model. First of all, using the crude estimates provided by George Woodwell, we have assumed that the increase in photosynthesis amounts to 5% for each 10% increase in the carbon dioxide content of the troposphere. However, this is applicable to only one-half of the land biosphere since the other half is assumed nutrient or water limited. This factor ($0.5 \times 0.5 = 0.25$) allows for an increase in the CO_2 content of the biosphere; without it a steady state would exist in the biospheric carbon irrespective of the atmospheric growth. Second is a buffering effect of the oceans. Suppose that the exchangeable carbon mass in the mixed layer (isolated from the deep ocean) equals that of the air. Then for every 11 units of carbon dioxide added to the atmosphere, 10 remain airborne and only 1 goes into the ocean instead of the 50–50 split expected by their carbon masses. However, the $^{14}CO_2$ is added in exceedingly low quantities, so that its buffering effect is unimportant and has been neglected.

SENSITIVITY TESTS

Sensitivity tests have been performed on various doubtful components of the model. In these tests, however, we must remember that whatever model is chosen must account for the full decrease in the $^{14}CO_2$ evident in the nontesting period of Fig. 3. Should the biosphere be eliminated, for example, then the oceans must compensate for its omission. Later, when the model is applied to the fossil-fuel CO_2, the oceans, in our example, will partially fulfill the role of the neglected biosphere.

In the sensitivity tests the biosphere has been omitted, the NPP doubled, the long-term biosphere altered from a 40- to a 20-year return time, and the growth limitation reduced to 0.05 rather than 0.25. In the oceans the buffering factor has been reduced to 6 and increased to 14 rather than the 10 in the model, and the deep oceans are assumed to be only 400 rather than 1600 years old. The changes in the forecast of the CO_2 concentration in the year 2000 generally lie within ±10 ppM, which is not significant in the light of the uncertainties (to be discussed in the following paragraphs) of converting the CO_2 predicted concentration into a climatic forecast.

However, these sensitivity tests of changes in the model reflect but the tip of the iceberg of uncertainty in predicting future levels of CO_2. It is naively assumed in these tests that the history of the atmosphere–biosphere–ocean transfers found in the 1950s and 1960s have and will be applicable from 1860 to 2000. This is hardly likely to be the case. In fact, year-to-year differences exist between the simple-model predictions and the Mauna Loa observations. Put another way, the model presumes, in effect, that about 60 to 65% of the fossil-fuel CO_2 will remain airborne each year. But in the mid-1960s this observed percentage dipped below 40 and, in very recent years, rose to well over 60, assuming that the Mauna Loa annual increments are representative of those for the globe. If these changes in the airborne percentage are indeed valid, there are significant year-to-year changes in the uptake by the biosphere and oceans.

To more clearly make this point, we compare the CO_2 photosynthetic uptake with fossil-fuel emissions. From Fig. 2, there are 5.6 or 7.6×10^{16} g of carbon taken up (and presumably released by respiration and decay) each year, depending on whether we want to include the very uncertain marine NPP. This is about 15 to 20 times greater than the 1969 fossil-fuel CO_2 releases. Thus a 1% decrease in the photosynthetic uptake due to droughts or other factors would appear as a 15 to 20% increase in the airborne fossil-fuel CO_2. Do we know that the year-to-year values of global NPP will not change by 1%?

Assuming that the atmosphere comes into equilibrium with the sea-surface partial pressure of CO_2, we can argue that each 1°C warming of the ocean surface will increase the CO_2 content by as much as 10 ppM. A global warming of the ocean temperature of only 0.1°C could possibly equal the current annual increment of CO_2 in the air.

These comparisons suggest strongly that the biosphere and oceans play so vital a role in the changes in atmospheric CO_2 content that small changes in their behavior can easily modify the predictions from the simple model calibrated from conditions in the 1950s and 1960s.

CLIMATE PREDICTION

An even larger measure of uncertainty must be attached to the prediction of climatic changes from an increase in atmospheric CO_2. It is well known that CO_2 absorbs short-wave solar wavelengths poorly but long-wave terrestrial wavelengths effectively. Thus solar radiation can reach the earth unattenuated by any increase in CO_2 concentrations, but the long-wave terrestrial radiation will be absorbed and partly emitted back to the lower atmosphere. The result is the greenhouse effect. But the analogy between an atmosphere with enhanced absorbers of long-wave radiation and a greenhouse is not good, because the glass inhibits turbulent transfer of heat. Further, CO_2 in the air always cools the atmosphere, but more CO_2 cools the lower atmosphere less while cooling the high atmosphere more.

The response of the atmosphere to changes in the radiation distribution is very complex, and a fully evolved model to simulate the climatic change does not now exist. What can be reported are only approximations to the true atmospheric adjustment to increasing CO_2 concentrations. Radiative transfer theory is reasonably well established. But the dynamic responses, air movements and energy transfers, are much more difficult to recreate. Perhaps most important, the changes in cloudiness that represent a dominant influence on the global heat budget may be modified in a manner as yet unpredictable.

The Manabe and Wetherald[6] study is most often quoted as the best one currently available on the change in temperatures from the addition of CO_2 from a one-dimensional (vertical) model. Figure 5 shows the relation between atmospheric CO_2 content in parts per million to change in global surface temperature away from the current 320 ppM. The prediction of 385 ppM in the year 2000 calls for a warming of about 0.5°C. A slightly different radiative treatment reduces the warming by about 30%. The model on which this forecast is based allows for new radiative temperature changes for increasing CO_2 but a constant relative humidity to try to cope with the added moisture that warmer air can hold. However, the average cloudiness employed in the calculations does not change when the air warms or cools. The model also produces much greater cooling in the high atmosphere than warming near the ground.

Manabe[7] has recently reported on some calculations using a three-dimensional model comparing climatic conditions with a doubling of the current CO_2 atmospheric composition. No ocean circulation is admitted, and a perpetual winter is prescribed. Further, there is still no change in the cloudiness even when the atmospheric humidity changes in response to the heating by the added CO_2. The result suggests a slightly greater global warming in the lower atmosphere than Manabe and Wetherald found in their one-dimensional case. But most dramatic is the much larger warming of the Arctic than might have been expected. The high latitudes warm twice as much as the globe as a whole. This is due to the marked thermal stability of the Arctic lower atmosphere in winter and the recession of the ice with the added warmth of the air. This calculation should not be treated literally but is suggestive of the fragility of the Arctic region to climate changes.

Indeed the cooling that has been in progress since the mid-1940s in the Northern Hemisphere has been concentrated almost entirely in the Arctic (north of 50°) and in the winter half-year. This cooling has proceeded despite the rapid increase in CO_2 evident in the atmospheric concentration. One must recognize that other factors besides CO_2 are responsible for the global climate; in all likelihood natural fluctuations, as yet not understood, play a dominant role since climatic fluctuations occurred long before man had his present technological powers and numbers.

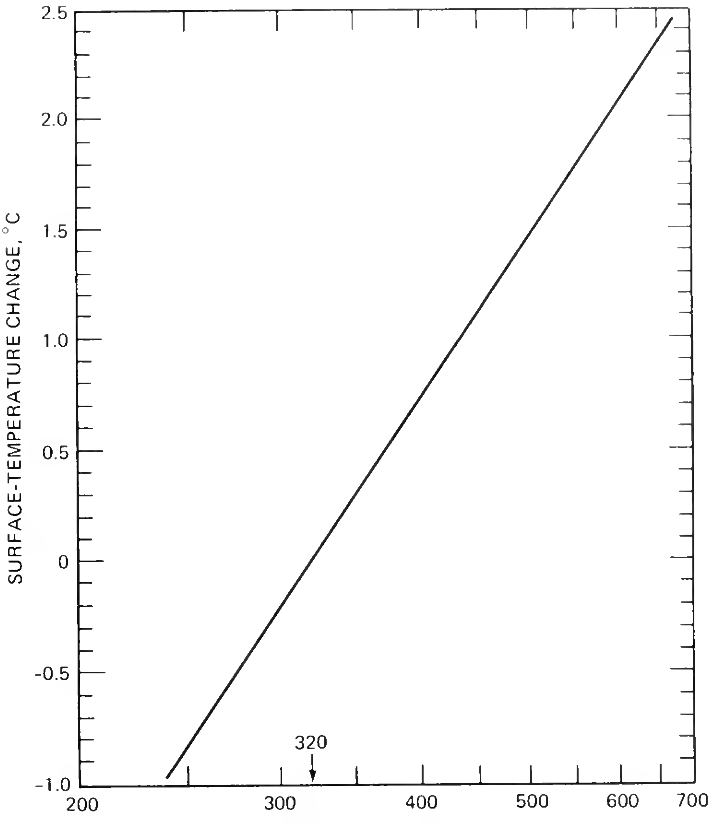

Fig. 5 Surface air-temperature change due to increased atmospheric CO_2 with average cloudiness, assuming a convective-radiation equilibrium and a fixed humidity (adapted from Manabe and Wetherald[6]).

There are at least two feedback mechanisms that have so far been omitted in quantitative treatments of climatic changes from increased CO_2. First, the added moisture may increase the cloudiness. Clouds play a dominant role in controlling the earth's albedo or reflecting power to solar radiation. It has been estimated that the net effect of a global increase of only 0.6% in low cloudiness over the globe will cool the lower atmosphere by the same 0.5°C that the 385 ppM is predicted to warm the lower atmosphere.[8] Thus, if the added warmth and moisture by the so-called greenhouse effect also increase low cloudiness, much of the warming can be negated.

The second is a positive rather than a negative feedback. If the warming of the lower atmosphere should also warm the surface layers of the waters, additional oceanic CO_2 will be released. This, in turn, would intensify the atmospheric warming and so forth.

At this time, I feel we are in a less confident position to forecast the future climate due to the combustion of fossil fuels than to estimate the increase in atmospheric CO_2 concentrations.

ACKNOWLEDGMENT

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DISCUSSION BY ATTENDEES

Wallis: If we disallow changes in the accumulation of carbon in the biomass, would you speculate on the climatic change that this would introduce into your model?

Machta: A run on the computer with all model parameters repeated except for the biota (i.e., no fossil-fuel CO_2 enters the biota) predicts an increase in atmospheric CO_2 concentration by the year 2000 of 394 ppM rather than 386. The increased CO_2 concentration of 8 ppM according to Manabe and Wetherald's calculation (Fig. 5 of my paper) will result in an additional warming of less than 0.1°C, which is well within the uncertainty of the climatic prediction.

Deevey: There is a third box between the atmosphere and the deep ocean, i.e., humus, which has a size about the same as the biota and the mixed ocean layer. Residence time in humus is of the order of hundreds of years. Would your results be significantly influenced by the addition of such a box?

Machta: Qualitatively, the additional removal of fossil-fuel CO_2 into the humus would decrease the atmospheric growth rate in the model and thus improve the fit between the 1958 to 1970 increment of 9 ppM observed at Mauna Loa with that of the model estimate of 12 ppM. However, over 10% of the total net primary production of the land biota would have to be transferred to the humus to reduce significantly the 12 ppM increment in model calculations.

Shotkin: Would you care to speculate on what mechanisms in the atmosphere might be responsible for the temperature decrease observed over the last 25 years?

Machta: Dr. Murray Mitchell is in the audience and is much better able to answer the question than I.

Mitchell: Of course I do not really know what is responsible for the cooling, but I have the feeling that part of the answer lies in the accelerated pace of explosive volcanic eruptions we have had in the tropics during the past quarter century. These eruptions have pumped a lot of tephra into the middle stratosphere after a hiatus of two or three decades. Dust at those altitudes tends to backscatter a significant fraction of solar radiation to space and therefore decreases the solar heating near the ground. Since the dust particles are too small to affect appreciably the long-wave terrestrial radiation escaping from below, the net effect of the dust is to cool climate. Other factors may enter the picture too. For example, anomalous long-period thermal interactions between the oceans and the atmosphere might account for part of the cooling, but I really cannot say what these interactions look like or precisely how they operate.

I should add something else. You have probably heard claims recently that the increasing dust loading of the atmosphere from human activities may account for the cooling. When dust enters the atmosphere from sources near the surface, the situation is not the same as that of stratospheric dust injections from volcanoes. Here it becomes crucial to know how efficiently the dust absorbs solar radiation as well as how much radiation it backscatters. The fact is, we do not know enough about the optical properties of anthropogenic dust to determine whether it is tending to cool the earth or to warm it up. So to blame the cooling trend on increasing atmospheric turbidity from man's activities is a bit premature.

FACTORS CONTROLLING CO_2 CONTENT IN THE OCEANS AND ATMOSPHERE*

WALLACE S. BROECKER†
Lamont–Doherty Geological Observatory of Columbia University,
Palisades Park, New York

This is a summary of what I think to be factors controlling the long-term carbon content of the atmosphere and the ocean, and I will begin with the grand carbon cycle (Fig. 1). We know that the main supply of carbon to the earth's surface is by erosion and metamorphism of sediments. The contribution of new carbon coming in from outer space or from deep in the mantle is probably very small. There are roughly 10^7 moles of carbon per square meter of ocean surface stored in sediments in the form of calcite, dolomite, and organic material which oil geologists call kerogen; in the ocean we have about one-thousandth as much. This carbon is being run around the ocean-sediment cycle at something that approaches steady state. At any given time one part in one thousand of the carbon is in the ocean–atmosphere system, and the rest is in sedimentary rocks. The distribution between these two reservoirs is determined by the time constants for the processes which destroy sediments and for those which remove things from the ocean. We know that the time constant for destruction of

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**Author's Note:* This paper is an edited transcript of my oral presentation. If the reader wishes a more detailed presentation of the ideas briefly outlined here, I suggest the following papers. First a treatment of the ocean chemistry control model is given in an article entitled "A Kinetic Model for the Chemical Composition of Seawater" published in *Quaternary Research,* 1: 188-207 (1971). The means by which paleoocean chemistry might be read from sediments are outlined briefly in this same paper and in more detail in a paper entitled "Calcite Accumulation Rates and Glacial to Interglacial Changes in Oceanic Mixing" that appears in a volume entitled *The Late Cenozoic Glacial Ages,* pp. 239-265, Yale University Press, New Haven, Conn., 1971. Finally the East Pacific Rise study is in press in a SEPM volume, suggested title *Studies in Paleo-Oceanography,* William Hay (Ed.).

†Lamont–Doherty Geological Observatory Contribution No. 1976.

sediments is on the order of one hundred million years. This time constant is dictated mainly by the great plate motions on the surface of the earth. The other important time constant is the residence time of carbon in the ocean–atmosphere system. How long does it remain in this system before being removed? We know from the amount of carbon in the ocean–atmosphere system and by rough estimates of how much is being added by rivers to the sea that it remains for about one hundred thousand years. Once trapped in the sediments, a carbon atom remains there 10^8 years, and, when finally released, it remains in the ocean only 10^5 years before being removed. If we run carbon around such a cycle, we will come up with a distribution coefficient of one part in the ocean–atmosphere reservoir to one thousand parts in the sediments. By contrast, chloride, which is very soluble in the sea and has a very low probability of removal, is roughly equally distributed between the sea and the sediments with about a 10^8-year residence time in sediments and roughly a 10^8-year residence time in the sea.

What goes on during the 10^5 years that a carbon atom spends in the ocean–atmosphere system? To understand this we must have some idea of the carbon cycle within the ocean. We will ignore the atmosphere to a large extent because I feel that for time scales of hundreds of years or more, the atmosphere is largely at the mercy of the ocean. The ocean dictates to the atmosphere what its CO_2 content should be. It is only when we have short-term transients (such as the current consumption of fossil fuels) that the atmosphere plays an important role.

We can view ocean circulation in terms of a two-box model consisting of a warm surface ocean and a cold deep ocean separated by the main thermocline—that region where the temperature goes from about 20°C to an average of about 2°C (Fig. 2). We find that across this boundary the largest chemical differences occur. For instance, there is about 20% more carbon dissolved in cold, deep water than in warm surface water. In deep Atlantic water, which is one of the main suppliers for the Pacific Ocean, dissolved carbon content is intermediate between the surface value and the deep Pacific value. This carbon distribution in the ocean is created by the interaction between the main circulation cycle and the biological cycle. The mixing cycle consists of a northward flow of surface water through the Atlantic toward the polar regions where it is cooled and sent into the deep sea. This water then travels around the ocean, down the Atlantic, around Africa into the Indian Ocean, and into and up the Pacific. As it goes, it upwells more or less uniformly. The deep current is depleted by the upwelling that Stuiver spoke of in his advection–diffusion model. The formation of deep water is localized in a small area, and upwelling occurs over a broad area of the ocean. Interacting with this mixing cycle is a particulate cycle. Plants manufacture various kinds of matter in the surface water, and, although much of this debris is degraded by animals living in the same water, perhaps 10 to 20% falls through the main thermocline into the deep sea. This is why the deep sea is enriched in most chemical properties with respect

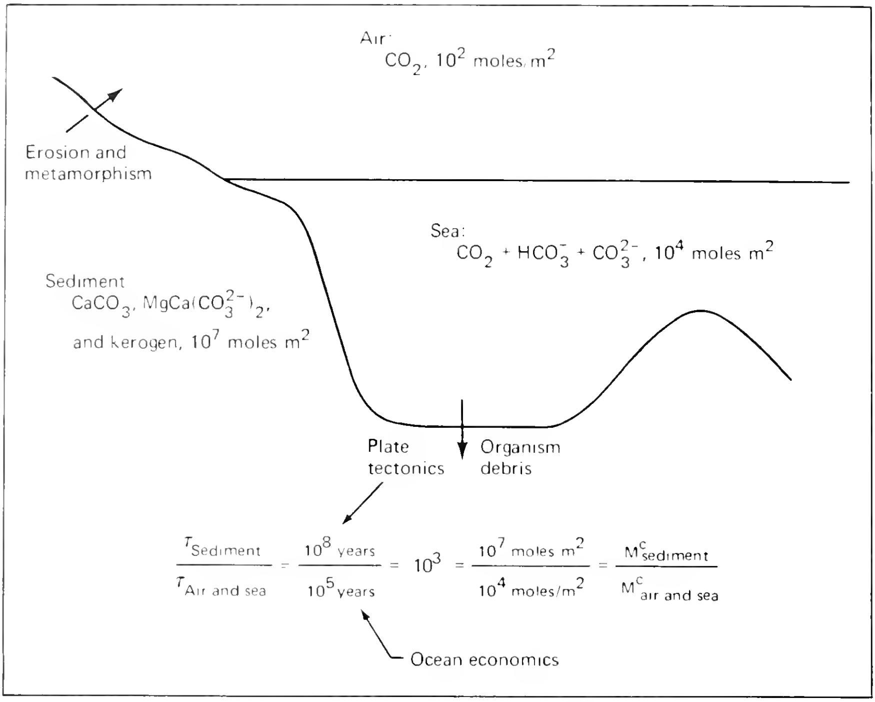

Fig. 1 The carbon cycle of the earth.

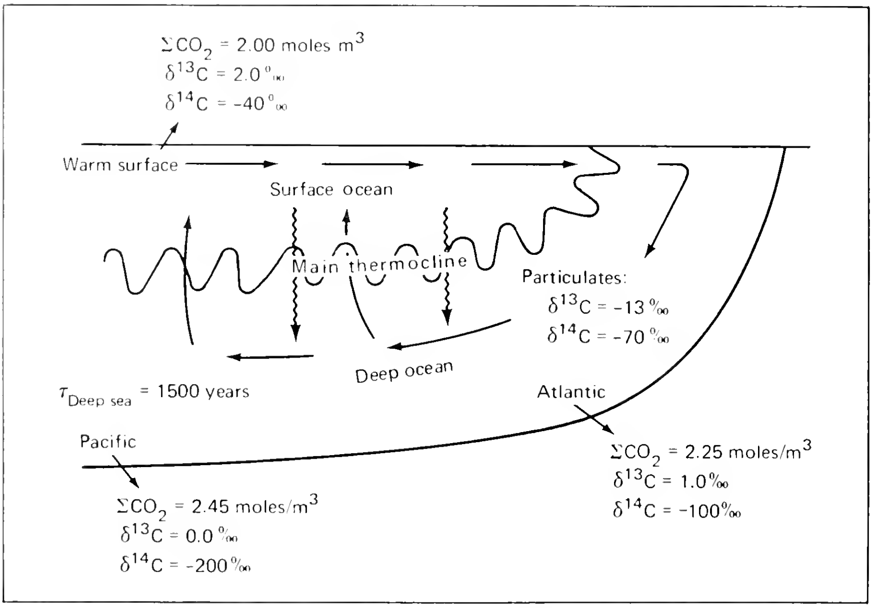

Fig. 2 The carbon cycle of the ocean.

to surface water. Oxygen would show the reverse effect because it is being consumed rather than manufactured in the deep sea. The enrichment around the deep ocean from Atlantic to Pacific results from the fact that the major source of deep water in the world ocean today is at the north end of the Atlantic. Water is being pushed around to the Pacific, and it tends to add to the vertical gradient of chemical properties a horizontal gradient giving the deep Pacific the highest concentration. The horizontal gradient builds up until "leakage" via eddies and minor currents matches the export by the main deep current. The main way in which carbon gets out of the ocean is with these organic particles, although this matter is, to a very large extent destroyed, about 1% gets into the sediment and is lost. Some of this carbon leaves as kerogen (~10%); the rest is removed from the ocean in the form of calcium carbonate. About 85% of the $CaCO_3$ produced in the sea is destroyed in the deep sea by dissolution, and about 15% is buried in the sediments. For organic tissue about 99% is destroyed, and only 1% becomes kerogen.

The decrease between deep and surface ocean is most dramatic for the nutrient elements phosphorus and nitrogen. They drop off by a very large factor and leave a residue in the surface ocean of only a few percent of the deep-water value. Silica is also greatly reduced in concentration through the action of diatoms which, given enough silica, would probably take over the aquatic plant world. By comparison the decrease for total dissolved carbon is only 15% and for calcium (a constituent of calcium carbonate), only about 1%. This results from the fact that, when deep water upwells to the surface, the life forces there quickly combine the critical nutrients, nitrogen and phosphorus, into organic matter. To do so requires one hundred or so carbon atoms for each phosphorus atom. Some of these organisms also need calcium carbonate to house themselves. One group of plants called coccoliths makes little calcite cages, and, of course, many of the animal plankton make calcium carbonate shells. As far as we know, for every hundred units of carbon in surface water which falls as organic tissue, 30 units fall as calcium carbonate. The amount of carbon going into organic tissue is dictated by the amount of phosphorus and by the normal chemical composition of plant matter (Fig. 3). This composition is pretty much the same through all fresh or marine aquatic organisms and seems to be a fundamental constant of life.

The silica goes into opal, some of which is produced by plants and some by animals that house themselves in opal instead of calcium carbonate. They use whatever silica is available along with the necessary amount of nitrogen and phosphorus. When silica runs out, the rest of the nitrogen and phosphorus, as well as that recycled within the surface sea, is used by other organisms. I will attempt to show that it is the economics of these elements that control the oceanic (and hence atmospheric) carbon cycle.

Carbon has a residence time in the ocean of only about a hundred thousand years. That means that every hundred thousand years we have had a completely

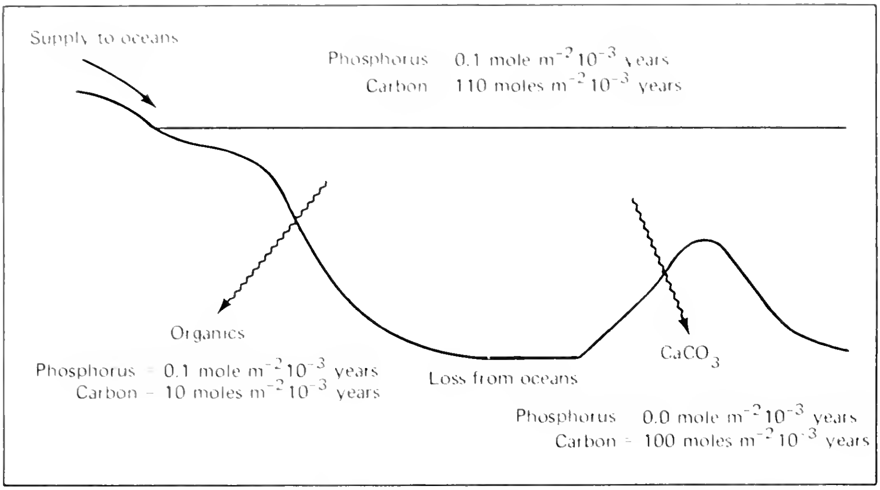

Fig. 3 The fate of carbon added to the sea. Fraction of carbon lost as organic tissue controlled by the availability of phosphorus.

different group of carbon atoms there. Therefore the system must be matching loss to input on that time scale. This is not to say that there cannot be fluctuations. There probably have been, but each hundred thousand years' input must have roughly equalled output if the system is to be considered anywhere near steady state. Later I will present data which show that over the past ten million years or so the system has been rather close to steady state. Consider now the input of carbon and phosphorus. Phosphorus is really god of the plant world because it is the only nutrient that is totally limited. There is controversy in this regard in biology. There are people who say that it is nitrogen that is limiting. I choose phosphorus because nitrogen is available in large quantities from atmospheric N_2.

The ratio of carbon to phosphorus coming into the ocean from erosion is about 10 times higher than it is for organic matter. This means that, if carbon is being removed in the form of organic tissue of about the same composition as that in plants and animals, then only about 10% of the carbon can be carried away in this form. The other 90% must be going out as calcium carbonate. The best averages of the carbon composition for sediments of the last 300 to 400 million years show that roughly 85% of the carbon is stored in the form of calcium carbonate and 15% in the form of kerogen. How does the ocean manage now to get rid of the 90 of 100 units of carbon supplied by rivers that cannot go out in the form of organic material?

Organisms produce calcium carbonate at a rate of about five times the rate that carbon is being supplied for this purpose by rivers (Fig. 4). In other words, if all the calcium carbonate produced every year by organisms were to fall and be preserved in the sediments, then the ocean would be running a very large

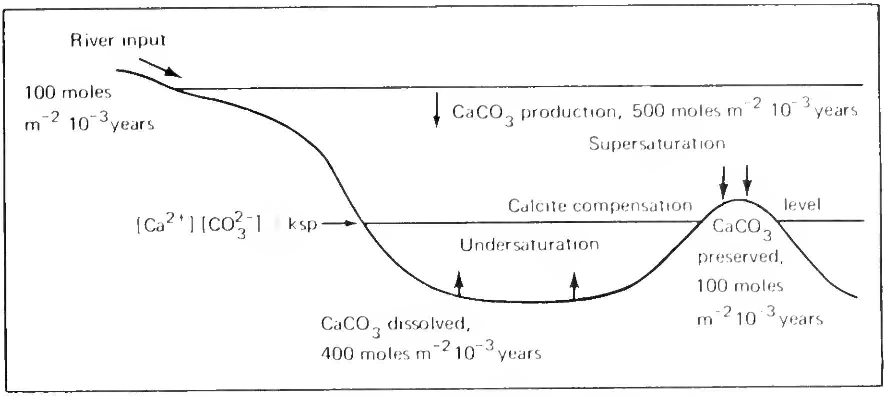

Fig. 4 The behavior of carbon in the sea. Carbonate-ion concentration at compensation level determined by carbon economics and calcium content of the sea.

carbon deficit that could not be maintained for long. The ocean solves this problem with a feedback mechanism which adjusts its chemistry such that roughly 80% of the ocean floor is bathed in waters corrosive to $CaCO_3$ (i.e., undersaturated); only 20% of the ocean floor is bathed in water that is supersaturated. The so-called calcium carbonate compensation level that separates sediments low in calcium carbonate from sediments rich in calcium carbonate can move up and down such that this overproduction is always taken back. We now have the major mechanism for carbon balance in the ocean. Carbon balance is controlled by bringing the carbonate-ion concentration to such a value that an appropriate fraction of the ocean floor is bathed in undersaturated water. If the ocean were to start disposing of too much of the calcium carbonate produced, the carbonate-ion content of the ocean would be lowered. The compensation level would then rise. Now the question is, "How do we know it is not the calcium content that changes?" On the time scale I am talking about, this would not be possible. Calcium has a residence time in the ocean of at least a million years, whereas the carbonate-ion adjustment time is roughly 10 thousand years. So, for any short transient, it will be the carbonate-ion content that adjusts and not the calcium content. The shape of the CO_3^{2-} vs. depth curve is fixed by the life and mixing cycles; the absolute value is fixed by the ocean's need to take back the right amount of calcium carbonate in order to keep its budget in balance. Now this alone does not determine the carbon content of the ocean because carbonate ion makes up only about 8% of the total dissolved carbon in the ocean. Most of the carbon is in the form of bicarbonate ion.

We have to fix one other parameter in this complex system. To do so we must consider the alkalinity of the ocean. We know that in the ocean there is a slight excess of major cations over the major anions. The excess (or alkalinity) is balanced by bicarbonate and carbonate. When a silicate rock that contains sodium, magnesium, calcium, or potassium dissolves and reaches the ocean, the anions balancing the cations will be bicarbonate or carbonate (instead of SiO_4^{4-} or OH^-). The ions in the rock, mainly silica, go into solution in neutral form and do not balance any charge. There can be OH^- ions balancing the charge, but OH^- combines rather rapidly with atmospheric CO_2 and makes bicarbonate; so it ends up that charge balance is accomplished by bicarbonate ion. The CO_2 from the air combines with rocks to release these cations; they are balanced in rivers by HCO_3^-. The silica goes down the rivers into the ocean in neutral form. In the ocean there must, on a fairly short time scale, be a means of removing these cations because at the rate at which these excess cations are entering the sea their excess (i.e., the oceans's alkalinity) would double every hundred thousand years. Therefore on a hundred thousand years' time scale, the ocean must be getting rid of these extra cations. Many people believe that there is some sort of reverse weathering process in operation; these ingredients are reacting somewhere in the pores of sediments to form minerals which, although not identical, would have the same bulk oxide composition as those which were being weathered. The critical thing here is that, if the CO_2 gas content of the entire ocean rises, then the CO_2 content of the atmosphere will rise and will in turn increase the rates of weathering and reduce the rates of precipitation into sediment pore waters. On the other hand, if the CO_2 content were lowered, it would reduce weathering rates and increase precipitation rates (Table 1). We could express this in terms of pH if so desired, but that would just be using another variable to say the same thing. What I suggest, then, is that the dissolved content of the ocean on a hundred thousand years' time scale must come to that value such that the gain and loss of the major cations are balanced (Table 2). If this is so, then we have fixed the chemical composition of the ocean. The carbonate ion is fixed by the economics of the element carbon; the CO_2 is fixed by the economics of the excess cations. Chemical equilibria within the ocean then fix the amount of bicarbonate: $CO_2 + CO_3^{2-} + H_2O \rightleftharpoons 2\ HCO_3^-$. Once we have fixed the amount of bicarbonate, we have fixed the pH: $CO_3^{2-} \rightleftharpoons H^+ + HCO_3^-$. Once we have fixed the amount of CO_2 in water in contact with the air, we have fixed the CO_2 content of the air. The carbonate alkalinity of ocean water is also fixed because it is the sum of the charges balanced by HCO_3^- and CO_3^{2-}. The total dissolved carbon content is the sum of the three carbon species (CO_2, HCO_3^-, CO_3^{2-}). If we fix carbonate ion and dissolved CO_2 contents, then we have fixed the carbon chemistry of the ocean–atmosphere system.

If the system operates in this way, then it is very sensitive to all sorts of environmental changes. If we were to double the rate of oceanic mixing, then we would bring up twice as much phosphorus, nitrogen, and silica, and life would respond, as we have seen in our lakes, to meet the challenge and fix all this material into plants. That would make twice as much debris falling down, the

TABLE 1

EXCESS CATION (ALKALINITY) CONTROL

$$\begin{aligned} \text{Alk} &= -Cl^- - 2SO_4^{2-} + \ldots + Na^+ + 2Mg^{2+} + 2Ca^{2+} - K^+ - \ldots \\ &= HCO_3 + 2CO_3^{2-} + H_2BO_3 + \ldots \end{aligned}$$

Example

Supply (Weathering)

$$\underset{\text{From atm}}{CO_2} + MgSiO_3 \Rightarrow Mg^{2+} + H_4SiO_4 + 2HCO_3$$

Loss (Unweathering)

$$Mg^{2+} + H_4SiO_4 + 2HCO_3 \Rightarrow \underset{\text{To atm}}{CO_2} + MgSiO_3$$

Rate increases with increasing $[CO_2]$; hence $[CO_2]$ of sea is fixed by cation economics.

Table 2

BALANCE OF MAJOR CATIONS IN THE OCEAN–ATMOSPHERE SYSTEM

$$[HCO_3] = \frac{\overset{\substack{\text{Carbon} \\ \text{economics}}}{[CO_3^{2-}]}\ \overset{\substack{\text{Cation} \\ \text{economics}}}{[H^+]}}{K_1^1}$$

$$[CO_2] = \frac{[HCO_3^-]\,[H^+]}{K_2^1}$$

$$pCO_2 = \frac{[CO_2]}{\alpha}$$

$$[\text{Alkalinity}] = 2[CO_3^{2-}] + [HCO_3^-]$$

$$[\text{Total } CO_2] = [CO_2] + [HCO_3^-] + [CO_3^{2-}]$$

exit rate of this material would double, and this would throw the ocean chemistry out of balance. Output would exceed input, and the concentration of all these limiting elements in the ocean would gradually drop down to half their value. At this point, input and loss would again match. With twice the upwelling rate and half the phosphorus content, the ocean would go back to the old productivity scheme and could balance river input by loss. If the amount of phosphorus coming in by rivers were to change, if the ecology of the ocean were to change, and if the oxygen content of the atmosphere were to change, the system would then be disrupted and the chemistry would move to a new set of values that would again exert economic control on the system.

Now let me mention residence times again. Residence time, or response time, is obtained by dividing the amount of an element dissolved in the ocean by the rate at which it is being added to the ocean. It can be thought of as replacement time (Table 3). For calcium this time is about a million years; for total dissolved carbon it is about a hundred thousand years; for phosphorus it is about 30 thousand years. Because carbonate ion is only about 7% of the total dissolved carbon in the sea, it responds 13 times more rapidly than the total dissolved carbon itself. It can adjust to balance input and loss in something like seven thousand years—a fraction of a glacial period. For the excess cations, alkalinity adjusts on the order of a hundred thousand years.

TABLE 3

REPLACEMENT TIMES IN YEARS
OF Ca, TOTAL CO_2, P, CO_3^{2-},
AND EXCESS CATIONS

	Replacement times, years
Ca	1,000,000
Total CO_2	100,000
P	30,000
CO_3^{2-}	7,000
Excess cations	100,000

We can look into the deep-sea sediments to see whether or not this system has been going along at a constant pace or whether it has been fluctuating. The major thing that has happened to our planet for the time scales in this discussion is, of course, glaciation. We have had one major climatic cycle every hundred thousand years. It would be interesting to see if there has been any major change in ocean chemistry as a result of these great climatic changes. Because what leaves the ocean has to equal what is coming in; looking at the bulk chemistry of sediments does not tell much about the chemistry of the ocean. The chemistry of the ocean is adapting itself to maintain throughput of this material. Thus different ocean chemistries may have been necessary at different times to dispense with the same input. The question then is, "What can be examined in deep-sea sediments that will provide the evidence we seek?" One interesting thing to look at would be the rate of calcium carbonate accumulation (Fig. 5). Some parts of the ocean floor are collecting all the calcium carbonate that falls. These places are flux monitors. In other places we are quite sure that much of what falls is dissolving, and what we are seeing is a record that has been distorted by subsequent dissolution of carbonate material. There are tests that can be applied to see whether this has happened or not. If the chemistry of the ocean is changing and the compensation level is going up and down, then we would

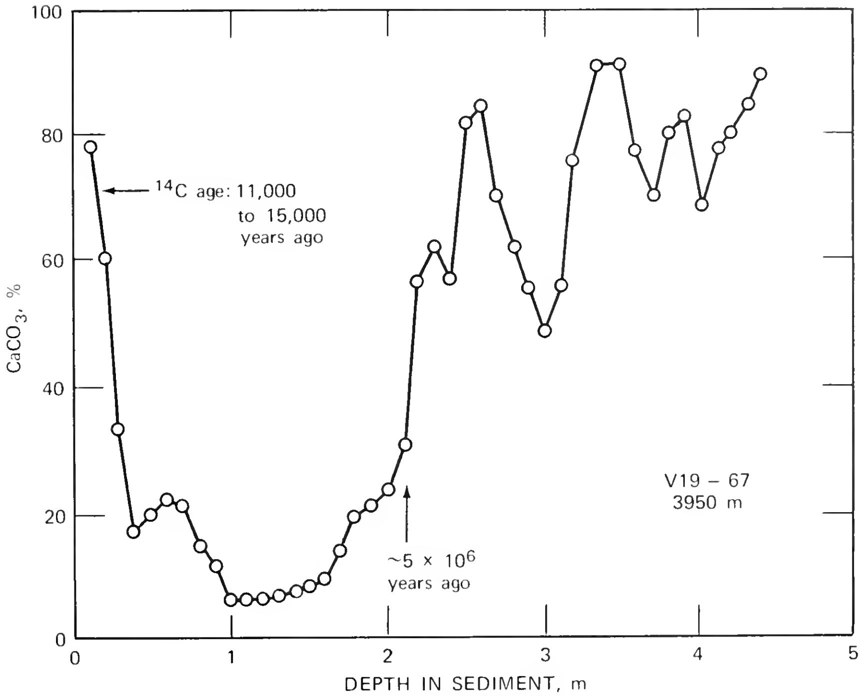

Fig. 5 Calcium carbonate as a function of depth in a sediment core from western flank of East Pacific Rise.

suspect that, when the compensation level was very shallow, calcium carbonate in sediments would be subjected on the average to a greater degree of dissolution than when the compensation level was deeper and the degree of solution less. We can look at different sediment columns for variations in the extent of dissolution.

One of the most interesting indicators of paleochemistry in the ocean is the ^{13}C to ^{12}C ratio in the calcium carbonate that is being deposited. There is a 2 per mil higher ^{13}C content in the dissolved carbon in warm surface water than there is in deep Pacific water, and, as is often the case, the Atlantic water falls roughly halfway between. The reason for this pattern is that the organic material being produced in this surface water is depleted in ^{13}C by 20 per mil by photosynthetic fractionation. It is leaving behind in the surface water carbon enriched in ^{13}C; the carbon that is carried down by mixing has to carry away more ^{13}C than the carbon that comes up in order to balance the fact that the carbon going out with the particles is deficient in ^{13}C. Calcium carbonate does not fractionate the carbon isotopes so that it does not alter the isotope ratio upon formation or dissolution. Roughly three-fourths of the particulate carbon is going down in the form or organic carbon (fractionated), and the other one-fourth is going down in the form of calcium carbonate (unfractionated).

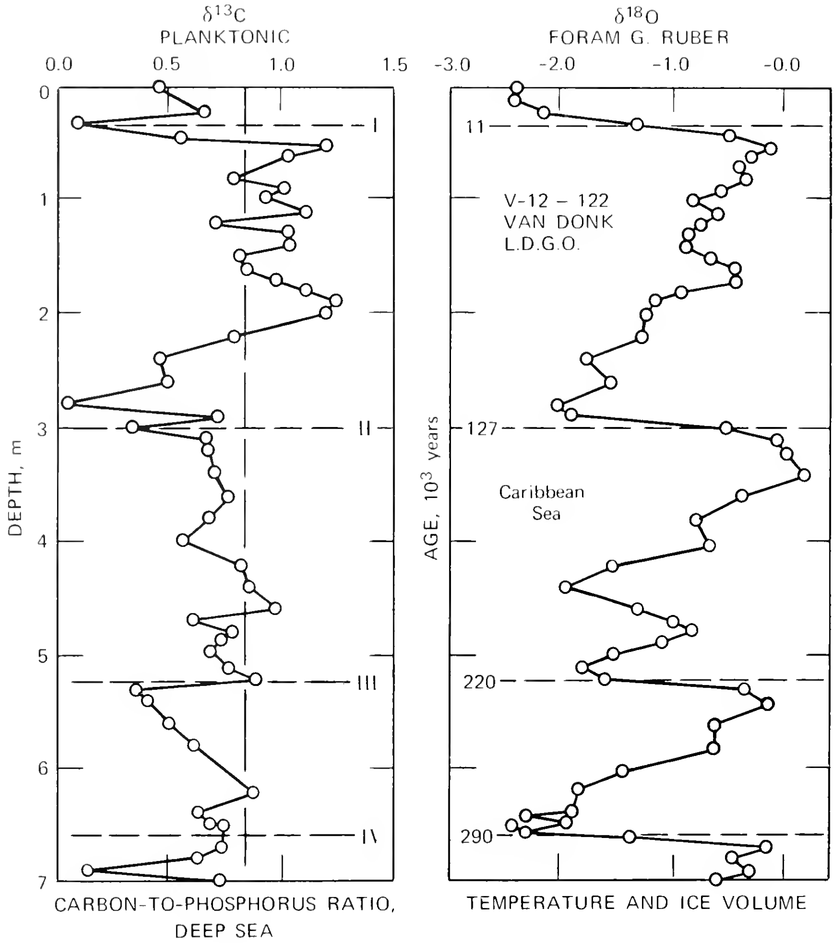

Fig. 6 The δ^{13}C and δ^{18}O ratio as a function of depth and age in a sediment core from the Caribbean Sea.

The difference of 2 per mil between surface and deep water is recorded by the forams that grow in these two reservoirs. Shells that grow in surface water record the ^{13}C in the surface ocean; shells that grow in deep water record ^{13}C at the bottom of the ocean. The difference between their ^{13}C contents is a reflection of the difference in the carbon isotope ratios in the dissolved carbon in the ocean. And that depends on the ratio of the phosphorus to carbon dissolved in the sea (Fig. 6).

One of the key factors in understanding paleochemistry is to ascertain the ratios of nutrient elements, one to another. First we will consider the calcium

TABLE 4

SEDIMENTATION RATE IN CARIBBEAN SEA

Core V12-122 Caribbean Sea	Sedimentation rate, $g/10^3$ years Cold (75 to 11)	Warm (127 to 75)
$CaCO_3$	1.6	1.5
Non-$CaCO_3$	0.8	0.9
Total	2.4	2.4
Forams	0.4	0.6
Coccoliths	1.2	0.9

carbonate accumulation rates. The best way to do this would be to make radiocarbon measurements in great detail through the late glacial and the postglacial periods. A very rapid warming from full glacial to full interglacial conditions occurred close to 11,000 years ago, but there really is not enough data to reach any conclusions. Where data exist, the accumulation rate is about twice as high for calcium carbonate in the late glacial as in the postglacial time. The number of locations is so small that I am not sure we can safely generalize. This is certainly something that should be done in more detail if we want to understand oceanic paleochemistry. I have chosen to take the oxygen-isotope curves for various deep-sea cores. Stratigraphic horizons and climatic horizons that can be recognized in these cores have been dated well in at least one core so that the age of these horizons is reasonably well fixed (Table 4). One such horizon is dated 11 thousand years ago, one 75 thousand years ago, and another is 127 thousand years. By taking the length of the intervals between these time horizons and dividing by the elapsed time, we can get rates of deposition. Then these rates can be broken down according to what the core is made of. When we do it for a core from the Caribbean Sea, we find that the average calcium carbonate accumulation rates during the warm part of the last interglacial period (127,000 to 75,000 years ago) and the cold part of the last glacial period (75,000 to 11,000 years ago) are roughly equal; the same is true for the noncarbonate material that, in this case, is largely dust probably blown off the continent or carried into the ocean by rivers. In this area the only difference noted in components is that the calcium carbonate deposited during the cold periods consists much more of plant calcium carbonate and less of animal calcium carbonate than in the warm periods. There is an ecologic change in that the plant population, the coccoliths, became a more important component and the animal population, the forams, a less important component in cold times. It is clear, then, that, if we want to do this study properly, we have to break this down into individual ecologic elements and look at absolute rates of each.

TABLE 5

SEDIMENTATION RATES IN VARIOUS OCEAN WATERS

Location	*	Sedimentation rates, (cm/10^3 years) Cocco-liths	Forams	$CaCO_3$	Non-$CaCO_3$	Total
North Atlantic	W	1.5	0.6	1.9	1.4	3.3
280	C	1.5	0.4	2.1	3.6	5.7
Caribbean	W	0.6	0.7	1.3	1.0	2.3
A240-MI	C	0.9	0.5	1.4	0.7	2.1
Equatorial Atlantic	W	1.2	0.9	2.1	1.0	3.1
A180-73	C	1.3	0.6	1.9	0.9	2.8
Equatorial Pacific†	W	0.75	0.08	0.83	0.35	1.18
RC11-209	C	0.75	0.25	1.00	0.15	1.15
Equatorial Indian†	W	0.4	0.3	0.7	1.2	1.9
IC-5	C	0.3	0.4	0.7	1.1	1.8

*W = warm = 127,000 to 75,000 years ago. C = cold = 75,000 to 11,000 years ago.
†Dissolution important.

It turns out that there are only about five areas where we have really good data (Table 5). If we focus our attention on the calcium carbonate total, we notice that in each of these areas the difference in accumulation rate between average glacial and average interglacial periods is discouragingly small. So the system appears to be reasonably stable. If we go on to dissolution evidence, we do see a difference. Everywhere we look, there is evidence of more severe dissolution of sediments during warm periods than during cold periods. For any place in the ocean for which we have data, apparently the sedimentary carbonate was more severely attacked by the waters at that spot during warm periods than during cold periods. One of the methods that is used is to look at the ratio of planktonic to benthic foraminifera in the sediments. Those which form on the bottom are hardy and do not dissolve very well, and those which grow on the surface are very fragile and dissolve very rapidly. When we subject a sediment to solution in the laboratory or in nature, the planktonics disappear rapidly and the benthics disappear slowly or not at all. The original value of the ratio is about 50 falling from the surface to 1 living on the bottom. The ratio is reasonable inasmuch as there is far more food available at the surface than there is at the bottom. In the equatorial Pacific Ocean, there is a band of carbonate sediment that is well below the compensation level. This sediment has been subject to intense dissolution. If no benthics were dissolved, we could say that about 95% of all the planktonic species had been destroyed by solution, during interglacial times, whereas during the cold period only 50% of the planktonics were dissolved. The same is true in the Indian Ocean; there is a much greater

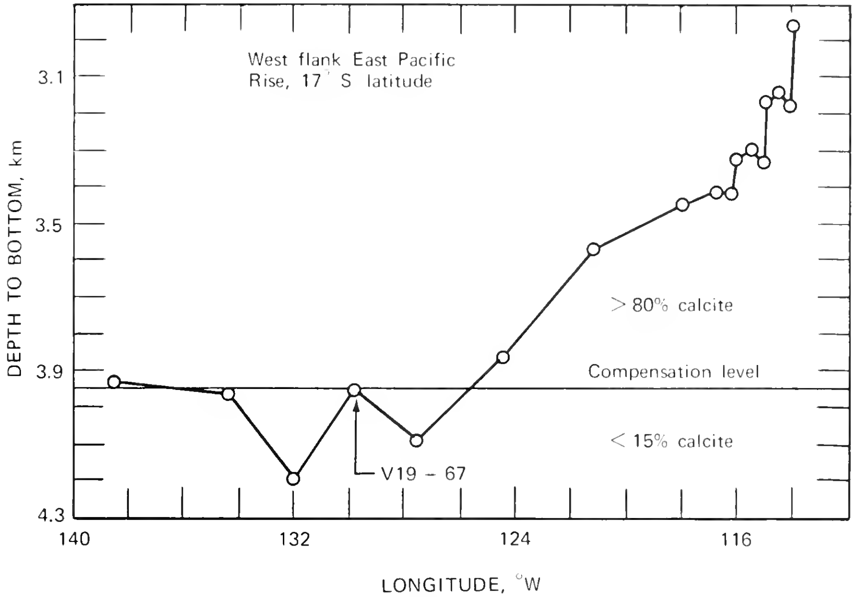

Fig. 7 The percent of calcite above and below the compensation level.

reduction in the planktonic-to-benthic ratio during interglacial times than during glacial times. In the Caribbean Sea the calcite component, which is the main component of the $CaCO_3$, is not dissolved during either period, but, in the glacial part of the section, aragonitic pterapods are found. Aragonitic calcium carbonate, which is a metastable, is 1.6 times more soluble than calcite. In today's Caribbean the pterapod shells that fall to the bottom are dissolving. During the peak of the last glacial period, pterapods accumulated in the Caribbean in great numbers, suggesting again that at the peak of the glacial period the compensation depth was deeper, subjecting the sediments to less solution. It is not clear why this happened. There are many possible explanations. For example, when the sea level went down during the glacial period, it cut off a tremendous amount of near-shore $CaCO_3$ production. The wide shelves were laid bare, and, of course, the calcium carbonate removed from the system on the shelves would have been cut way back.

A logical thing to do is to run an "uphill" traverse of cores right across this compensation level and look directly at the differences between cores from above the compensation level to cores below. Our geophysicists at Lamont once ran such a traverse for heat-flow study and got closely spaced cores on a traverse east from Tahiti to the crest of the East Pacific Rise about 17° south. We had been studying those cores and found a very dramatic thing; the cores down to about 3950 m are about 90% calcium carbonate; the cores below 3950 m are, on the average, less than 10% calcium carbonate (Fig. 7). To go from 90% to 10%, if the rate of influx of the dilutant, clay, iron, and manganese oxides, and opal is constant, requires a 100-fold change in the rate of calcium carbonate accumulation. So the change represents a 99% dissolution of the carbonate out of this sediment. It is quite interesting that one core shows no evidence of dissolution, and another, 50 m deeper, shows very strong evidence of dissolution, so that this boundary is, at least in this part of the ocean, remarkably sharp. Above the compensation level the carbonate content of the cores is amazingly uniform with depth. In fact, in one core, 60% of the material is calcium carbonate, and 40% is iron and manganese oxide that almost certainly comes out of the crest of the mid-ocean rise. So we have a core in which 40% of the material is related to vulcanism and 60% is related to productivity at the surface spanning 250,000 years. There is no change in this ratio. The carbonate content goes from 58% to 62% and just bounces around within those limits. This again is very interesting because it says that either there is coupling between vulcanism and productivity, which most people would say is madness, or much more likely neither of these processes has undergone an appreciable change in rate. Apparently these two processes are going on at roughly the same ratio right up to the present.

We will next discuss a core that has been subjected to intense dissolution. If we go deep enough in such a core, we come back to a high carbonate sediment. During the course of its history, each area went from above the $CaCO_3$ to below the $CaCO_3$ compensation level. The great oceanic plates that bear these sediments are not only moving away from the ridges at a rate of a few centimeters per year, they are also getting deeper. They go from 3000 m at their point of origin to about 6000 m at the trench into which they disappear at a rate of about 30 m/million years. At some point the plate drops through the compensation level, and calcium carbonate accumulation ceases.

Cores from below the compensation level show funny carbonate tails at their tops. We first postulated that they represented kinetic lag; the carbonate takes an average of 15,000 years to dissolve. This seemed true until we did radiocarbon dating and found that the top point in the piston core and in the trigger weight core give an age of 11,000 years. This may indicate that, during the last glacial period, there was a high influx of carbonate that did not dissolve at this point in the ocean. Probably these high carbonate peaks indicate that during the height of the last glaciation the compensation level dropped a couple of hundred meters or so and permitted carbonate to accumulate in regions of the ocean floor where it is not accumulating today. So we see from the dissolution phenomena that there was a change in compensation level corresponding to times of glaciation.

Now for the last method, the method based on ^{13}C. To review what was said before, there is a difference between ^{13}C content of surface Pacific carbon and deep Pacific carbon today of about 2 per mil (Table 6). This is reflected by the

TABLE 6

CONTROL ON OCEANIC ^{13}C DISTRIBUTION

$$\partial^{13}C_{\substack{\text{Warm}\\\text{surface}\\\text{water}}} - \partial^{13}C_{\substack{\text{Pacific}\\\text{deep}\\\text{water}}} = \Delta_{\substack{\text{Warm surface}\\\text{water,}\\\text{organic debris}}} \frac{\text{Carbon to phosphorus, organic debris}}{\text{Carbon to phosphorus, deep sea}}$$

$$= 20\text{‰}\,\frac{100}{1000}$$

$$= 2\text{‰}$$

$$\partial^{13}C_{\substack{\text{Plankton}\\\text{forams}}} - \partial^{13}C_{\substack{\text{Benthic}\\\text{forams}}} \cong \partial^{13}C_{\substack{\text{Warm surface}\\\text{water}}} - \partial^{13}C_{\substack{\text{Pacific}\\\text{deep water}}}$$

^{13}C content of shells formed by planktonic and benthic organisms. It is likely that, if there is a temperature effect for carbon, it would be insignificant. The absolute fractionation for oxygen isotopes between water and forams is 40 per mil; for carbon, it is about 1 per mil. Hence temperature changes will not alter the planktonic–benthic carbon isotope difference. The thing that sets the magnitude of 2 per mil is the ratio of the carbon-to-phosphorus ratio in the organic debris to that of carbon-to-phosphorus ratio in the deep sea. This ratio fixes the fraction of the upwelling carbon that is fixed into organic debris and falls back into the deep sea as opposed to the fraction that rides back down with the water (or with the falling $CaCO_3$). Today about 10% of the carbon that comes up is needed by the organisms for their soft tissue; the other 90% is not needed because there are no nitrogen and phosphorus to match it. Therefore about 90% goes down with the water (or $CaCO_3$), and 10% goes down with the particles. That 10% that goes down with the soft-tissue particles has an average fractionation of 20 per mil. The resulting ^{13}C enrichment in the remaining carbon is 0.10 × 20, or 2%. If there was a time when the ratio of carbon to phosphorus was different than today, then it ought to be recorded by the ^{13}C difference between benthics and planktonics grown at that time. We will assume that over a period of a million years this carbon-to-phosphorus ratio demanded by marine organisms has not changed, and that if we do see ^{13}C differences, they are due to changes in carbon-to-phosphorus ratio in the sea. This has even broader implications because the major factor controlling the CO_2 content of the atmosphere is not the temperature changes or the salinity changes in the ocean due to glaciation. They are hardly worth mentioning when compared to the effects of changing the ratios of these nutrients. These nutrients all have time constants for replacement in the ocean of about a hundred thousand years, which is approximately the length of a glacial period. It is conceivable that the ratios could change considerably over the course of a single cycle. Suppose we bring up a parcel of deep water with a certain alkalinity and a certain total CO_2

TABLE 7

CHANGES IN RATIO OF TOTAL CARBON AND ALKALINITY AS DEEP WATER IS BROUGHT TO THE SURFACE

	Deep water*	After formation of organic tissue* →	After formation of $CaCO_3^*$
HCO_3^-	232	190	190
CO_3^{2-}	10	30	23
CO_2	3.0	0.7	0.9
Total CO_2	245	221	213
Alkalinity	252	252	236
$\frac{HCO_3^{-2}}{CO_2 \cdot CO_3^{2-}}$	1800	1800	1800

*In micromoles.

content. The equilibrium constant for that temperature (1800) demands that the speciation in the water be as follows: 232 micromoles of bicarbonate, 10 micromoles of carbonate, and 3 micromoles of dissolved CO_2 gas (Table 7). The first thing that happens to that water when it reaches the surface is that the plants take up all the nitrogen and phosphorus and an appropriate amount of carbon, leaving the water devoid of the nutrients and deficient in carbon. If there were no calcium carbonate production along with that, then the 10% removal of carbon would drop the carbon value by 10%. There is no alkalinity change associated with the formation of organic tissue, and the equilibrium constant would not change. From these parameters we could calculate the new distribution of species. What we see is that the carbonate ion goes up by a factor of 3 and the CO_2 content goes down by around a factor of 4. So if we were to have a Strangelove revolution, which wiped out all life, the surface ocean would then assume the chemistry of the deep sea (90% of the ocean). The deep sea has the chemical composition near the oceanic average, and the thin layer of water at the surface has a highly modified chemistry that is modified by the life cycles of the organisms. Interestingly enough, because of organic removal, the CO_2 content of surface ocean water is four times lower than it was in the upwelling water. It follows, then, that the CO_2 content of our atmosphere is four times lower than it would be in the absence of life. So we see life exerting a strong influence on the CO_2-content difference between these two reservoirs. When we add to this the effect of calcium carbonate removal, we find the opposite effect. When plants or animals manufacture calcium carbonate, they use not only carbon but alkalinity as well. They take out two plus charges (as Ca^{2+}) per carbon atom, and the alkalinity drops from 252 to 236. If we say that, for every 10 units of organic carbon that fall, 3 units of carbonate fall, we see that the CO_2 partial pressure is three times lower than it is in the deep sea because of life.

These things are all coupled together. Deep-sea water has a ratio of carbon to phosphorus ten times higher than organisms, and that is why only a small fraction of the carbon is used in the surface ocean. Because of this the difference in ^{13}C to ^{12}C is only 2 per mil, and the atmosphere has a CO_2 partial pressure of 320 rather than 1000 ppM. Suppose the $\partial\ ^{13}C$ difference were 4 mils in an ocean at some time past. Then the excess of carbon over that needed by phosphorus would be reduced by a factor of 2, and the CO_2 partial pressure would be even further depressed from the deep-sea value by another factor of 2 down to roughly 160 ppM. If we went the other way and had an even greater excess of carbon by a factor of 2 relative to phosphorus, the ^{13}C-to-^{12}C differences would be cut to 1 per mil and the CO_2 partial pressure would rise by a factor of 2 (to 640 ppM). What we find, then, is that the ocean is much more sensitive in its surface CO_2 content to the ratio of carbon to phosphorus than it is to other environmental parameters, such as temperature and salinity. In trying to measure the ^{13}C-to-^{12}C difference between benthic and planktonic forams of different ages, we find that measuring carbon in deep-sea cores is frustrating. Results from planktonics in a Caribbean core suggest that there is a distinct ^{13}C difference between the last glacial period and all the rest of time (including other cold periods). We have data on benthics during this period indicating that there was no change in the benthic composition; this would mean that the difference between planktonics and benthics was enhanced to about 2.5 per mil on the average, which would suggest lower CO_2 partial pressures in the atmosphere during the last glacial period.

In summary, this has been an attempt to show how one geochemist looks at the factors controlling carbon chemistry in the ocean and the conclusion is that it is very sensitive to the interaction between the life cycles and the mixing rate of the ocean and, therefore, potentially variable in time. Studies of deep-sea sediments may provide valuable clues as to the nature and magnitude of these changes and how they relate to the climatic history of the planet.

DISCUSSION BY ATTENDEES

Wetzel: Would you comment on your opinion of the interactions of dissolved organic compounds adsorbed to or coprecipitated with $CaCO_3$ in regard to inhibition of total dissolution of $CaCO_3$ on sedimentation?

Broecker: The kinetics of $CaCO_3$ deposition are fearfully complicated in the inorganic layer of the ocean and of solution are at least moderately complicated. There is a fantastic range of opinion on this subject—to some people what I have said in a sense is heresy, although my argument could be adapted to anybody's model of what is going on. I am trying to say that, if you go deep enough in the sea, there is a very strong tendency for carbonate to dissolve and that, if you stay shallow enough in the sea, there is a strong tendency for the carbonate to be preserved, and so you can jump over the details of the kinetics to make the broad statement. Now, if you want to make more detailed arguments, then you have to understand this, and I do not think people really understand it well enough to draw any conclusions.

Wetzel: A little more specifically, I was referring to the possibility of an inhibition of dissolution by certain types of organisms.

Broecker: It has been proposed that some calcium carbonate has a natural armoring of its own organic matrix or tissue, but I would not draw any conclusion at this point. A lot of experiments have been done, but no really unifying theory explains the model.

ATMOSPHERIC CARBON DIOXIDE AND RADIOCARBON IN THE NATURAL CARBON CYCLE: I. QUANTITATIVE DEDUCTIONS FROM RECORDS AT MAUNA LOA OBSERVATORY AND AT THE SOUTH POLE

CARL A. EKDAHL and CHARLES D. KEELING
Scripps Institution of Oceanography, University of California at San Diego,
La Jolla, California

ABSTRACT

The concentration of atmospheric CO_2 in the Northern Hemisphere increased by 6.8 ppM from 1959 to 1969, according to a long series of measurements at the Mauna Loa Observatory, Hawaii. In the same period the Southern Hemisphere concentration increased by 6.7 ppM, according to an even longer series of measurements of South Polar air. These increases, when averaged, correspond to 2.34% of the presumed preindustrial CO_2 concentration of 290 ppM and imply that approximately 49% of the contemporary production of CO_2 from combustion of fossil fuel and kilning of limestone remained airborne. The approximately 51% not remaining airborne was evidently incorporated into the oceans and land biota. To learn more about this uptake, we have taken into account atmospheric radiocarbon (^{14}C) variations as recorded in tree rings, and to interpret this record we have examined a series of geochemical models of the reservoirs into which CO_2 and ^{14}C can mix.

We established the essential character of these models by evaluating an analytically derived atmospheric transfer function for a wide range of linear-model parameters. For a purely oscillatory ^{14}C source, this function gives the attenuation and phase shift of $^{14}CO_2$ in the lower atmosphere; for a purely exponentially increasing CO_2 source, it gives the fraction of CO_2 remaining airborne or in the lower atmosphere. In both cases the source is assumed to have operated until initial transient variations have died out. For reasonable reservoir sizes and transfer times, the stratospheric (heliomagnetic) variation in $^{14}CO_2$, as estimated from direct observations of cosmic rays and sunspot numbers, is strongly attenuated in the lower atmosphere, whereas the predicted airborne fraction agrees with the earlier implied value of 49% (42% for the lower atmosphere) only if the carbon pool of the land biota grows appreciably. These models, with nonlinear corrections, are used in the paper following (part II of this study) to predict year-by-year simultaneous variations in atmospheric CO_2 and $^{14}CO_2$.

INTRODUCTION

A substantial portion of the carbon dioxide (CO_2) produced since the beginning of the industrial era by the combustion of fossil fuel (coal, petroleum, and natural gas) has accumulated in the atmosphere. The remainder has been taken up by the two other major pools in the short-term global carbon cycle—the oceans and the land biota (biosphere). Two long series of direct measurements of the rise in atmospheric carbon dioxide will now be used to establish the fraction of industrial CO_2 remaining airborne. Knowledge of this fraction and of spatial and temporal variations in natural radiocarbon will then be used in an attempt to estimate how much industrial CO_2 is taken up separately by the oceans and land biota.

A central problem in producing this estimate is to formulate a satisfactory model of the carbon cycle. The problem is difficult because certain experimental parameters cannot be determined accurately. The modeling problem will be considered in two parts. In the first, presented in this paper, two determinative attributes of the carbon cycle will be examined separately: (1) the ability of the atmosphere, coupled with the ocean and land biota, to attenuate stratospheric oscillations in natural radiocarbon and (2) the ability of the same reservoirs to redistribute an exponentially growing source of inactive industrial CO_2 injected into the lower atmosphere. We seek to establish how predictions of attenuation and redistribution are affected by assumed transfer times, reservoir sizes, and growth rates, when these parameters are varied over a wide range of values. By using a mathematical technique involving a transfer function (equivalent to an integral transform), we gain this information without solving completely the set of governing differential equations of the model under investigation.

In part II of this study, presented in the next paper,[1] the geochemical models examined in this paper are used together with estimates of the annual rates of production of radiocarbon and industrial CO_2 to make year-to-year predictions. These predictions are then compared with direct observations as a means of further testing of the models. Finally a narrow range of model parameters is selected and used in predicting future changes in the short-term global carbon cycle.

DIRECT MEASUREMENTS OF ATMOSPHERIC CO_2

Annual changes in atmospheric CO_2 concentration have been documented by Bolin and Bischof[2] using discrete-sample analysis of air collected on aircraft, as well as by Kelley[3] and Keeling[4,5] and their coworkers using continuous recording ground-based gas analyzers supplemented by discrete samples. The two longest and most continuous records will now be discussed in detail. Both records are extensions of earlier published data and are expressed on the basis of the same provisional absolute calibration.[6,7]

A nearly uninterrupted series of atmospheric CO_2 measurements made with a continuous CO_2 gas analyzer at the Mauna Loa high-altitude observatory on the island of Hawaii now extends over a period of 14 years. This record was gained by comparison of the concentration of atmospheric CO_2 up to 96 times per day with reference gas mixtures calibrated at the Scripps Institution of

Oceanography. Those data readily identified as contaminated by local biological, volcanic, or combustive activity were edited from the record. The remaining data were averaged first over each day and then by month. The course of the monthly mean concentration, expressed as a mixing ratio in parts per million by volume (ppm) (Fig. 1), reveals a seasonal variation of about 6 ppM, peak to peak, superimposed upon a secular increase of about 0.8 ppM per year. The former feature we ascribe to the seasonal growth and decay of the land biota and the latter feature to retention of industrial CO_2 in the atmosphere.

To establish the secular trend apart from the seasonal variations, we first fitted several trial functions to the monthly means by the method of least squares. Statistical tests of significance indicate that the best fit is achieved using an oscillating power function consisting of a third-order polynomial in time to represent the trend, plus sinusoidal terms representing 6- and 12-month oscillations.[4] The polynomial function is plotted in Fig. 2 along with the seasonally adjusted monthly average concentrations. It suggests that variations have occurred in the secular trend during the last decade. A 12-month moving average of the monthly means (Fig. 3) indicates essentially the same trend. The trend, derived by either of the foregoing methods, is probably close to the best available estimate of recent changes in atmospheric CO_2 in the Northern Hemisphere.

From measurements of CO_2 in air collected in 5-liter glass flasks twice per month at Amundsen–Scott station at the South Pole, the secular trend of atmospheric CO_2 for the polar Southern Hemisphere can also be estimated. The results constitute the longest modern record of atmospheric CO_2 variations at any single location. In addition to 1453 analyses of 749 flasks exposed on 291 sampling dates between 1957 and 1971, a gas analyzer at the station furnished continuous data from 1961 to 1963. Contaminated data were removed from the flask analysis record by rejecting analyses that were more than 1.25 times the standard deviation above an estimate of the mean provided by a least-squares fit of the same form of oscillating power function as that used for the Mauna Loa record. This procedure was reiterated until the originally skewed distribution resembled a normal distribution with a standard deviation approximately equal to the inherent precision of the sampling technique (0.30 ppM).[5] Several iterated rejections beyond the predetermined cutoff yielded no significant changes in either the dispersion of the retained data or the estimate of the secular trend.

The retained flask data (73% of the original data) were combined into averages for each sample date and these, together with the bimonthly continuous analyzer averages for 1961 and 1963, were fitted again to the oscillating power function used before (Fig. 4). The secular trend was abstracted as a third-order polynomial (Fig. 5). The South Pole and Mauna Loa trends when compared (Fig. 6) are very similar. The CO_2 concentration at the South Pole is systematically lower because the principal sources of industrial CO_2 occur in the Northern Hemisphere.

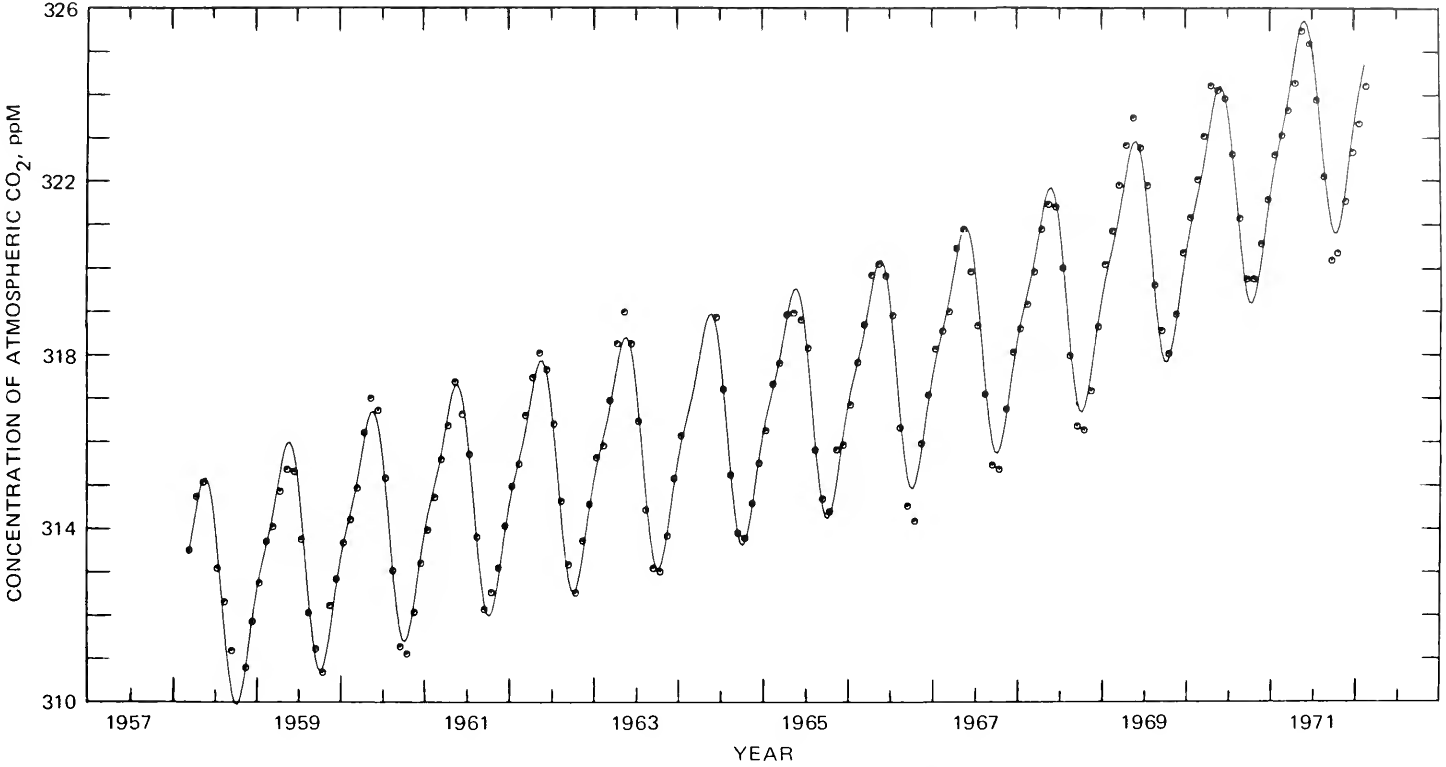

Fig. 1 Long-term variation in the concentration of atmospheric CO_2 at Mauna Loa Observatory. The circles indicate the observed monthly average concentration. The oscillatory curve is a least-squares fit to these averages of an empirical equation containing 6- and 12-month cyclic terms and a cubic-trend function, chosen to contain powers of time up to the third.

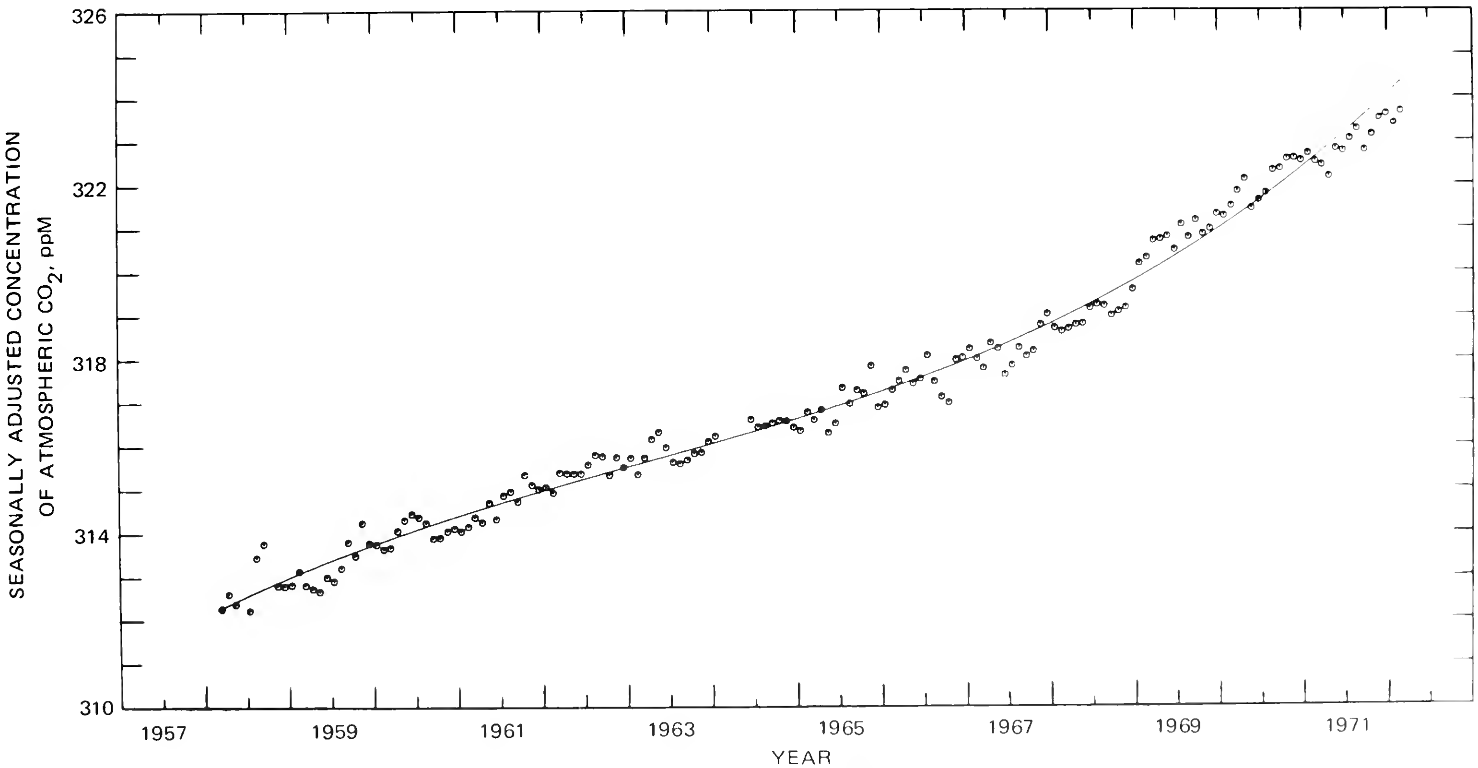

Fig. 2 Secular trend of atmospheric CO_2 concentration at Mauna Loa. Circles: monthly averages seasonally adjusted by subtracting the seasonal variation given by the 6- and 12-month cyclic terms used in deriving the curve of Fig. 1. The full curve is a plot of the cubic secular trend function used in deriving the curve of Fig. 1.

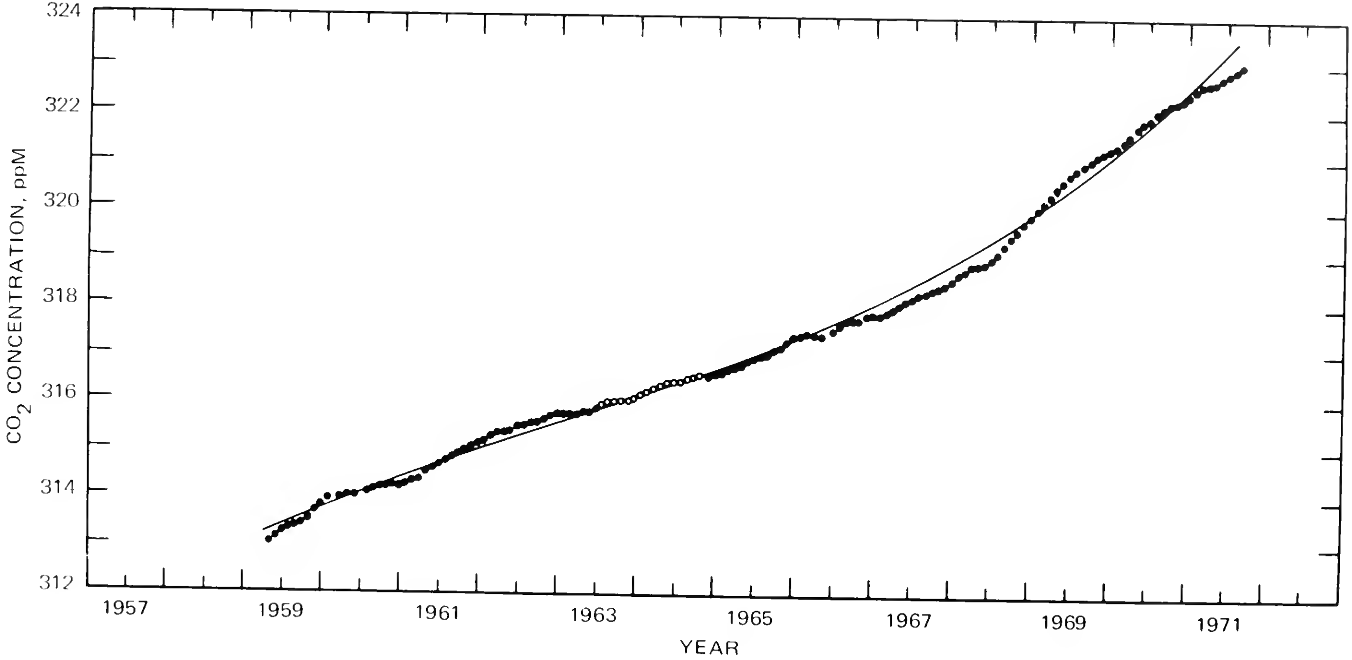

Fig. 3 Twelve-month moving average of the concentration of atmospheric CO_2 at Mauna Loa. Means, shown as circles, are plotted vs. the sixth month of the appropriate 12-month interval. For February to May 1964, because no data existed, monthly values of the CO_2 concentration were estimated from the empirical equation plotted in Fig. 1. Values of the moving average which depend on these estimated values are shown as open circles. The full curve indicates the secular trend function of Fig. 2, shown for comparison.

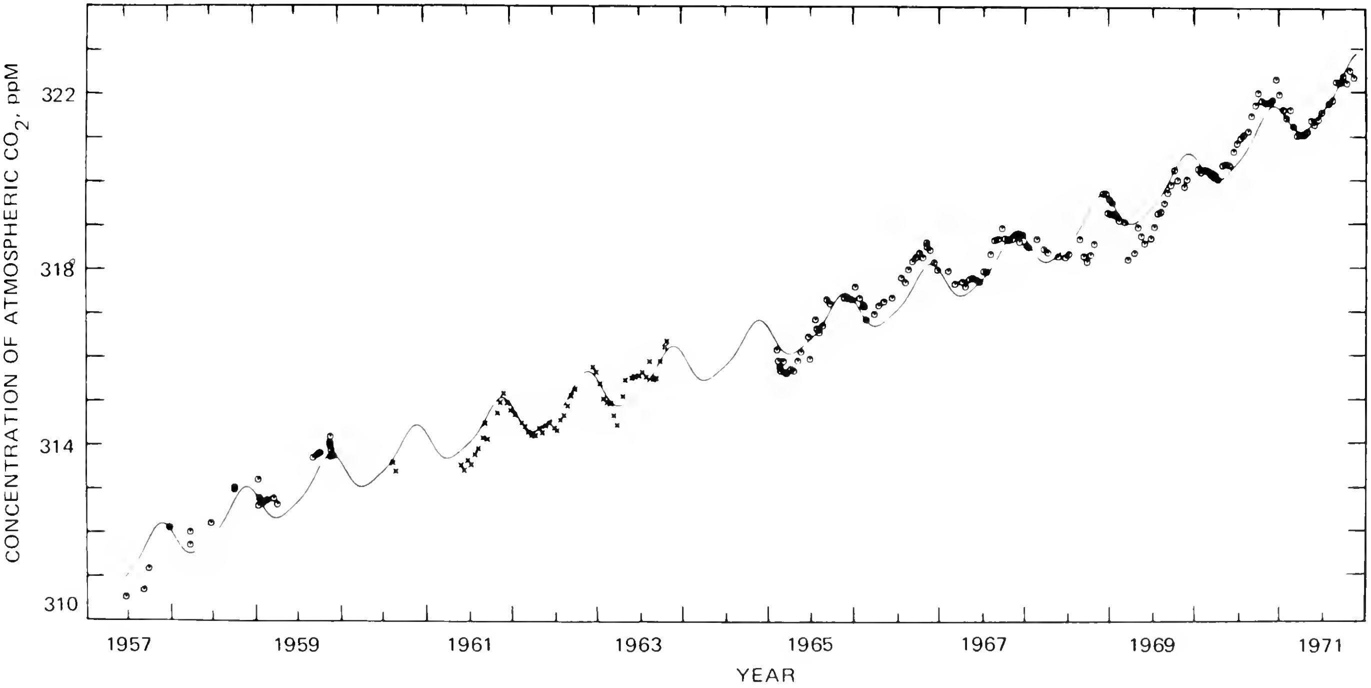

Fig. 4 Long-term variation in the concentration of atmospheric CO_2 at the South Pole. ⊙: daily averages based on flask analyses; x: continuous analyzer bimonthly averages. The oscillatory curve is a least-squares fit to these averages of an empirical equation having the same form as that used to derive the seasonal variation and trend for Mauna Loa (Fig. 1).

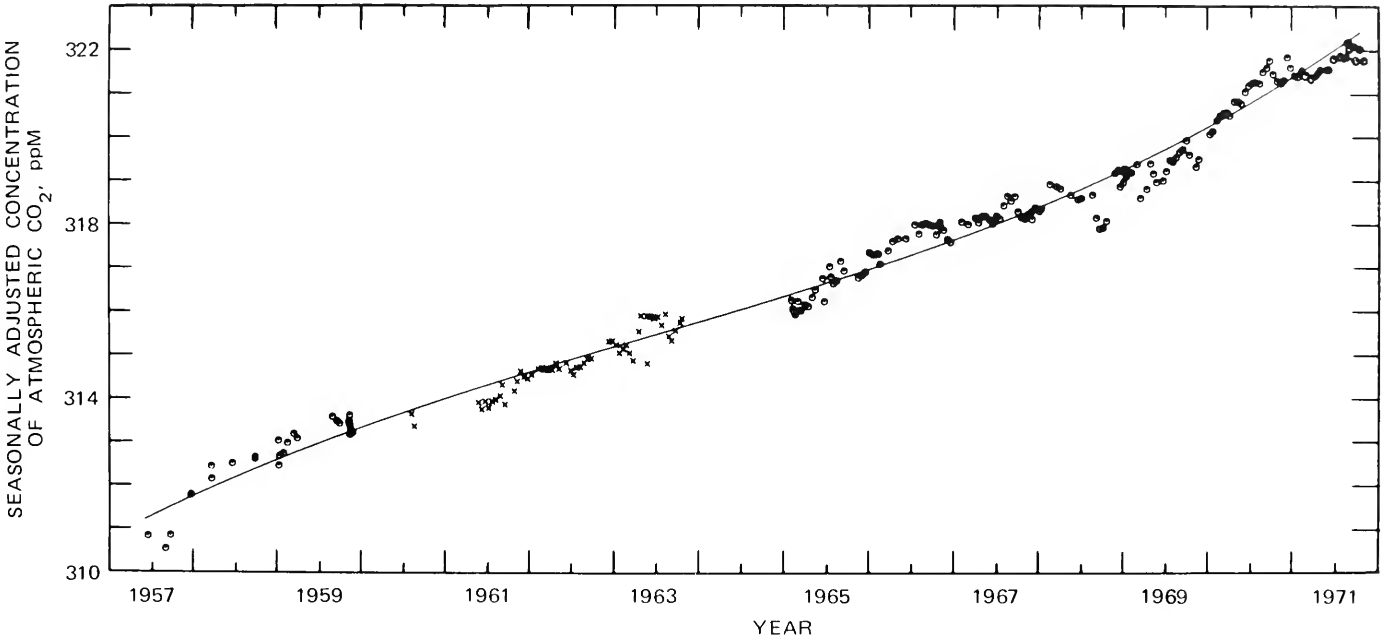

Fig. 5 Secular trend of atmospheric CO_2 at the South Pole. ⊙: daily flask averages seasonally adjusted by subtracting the seasonal variation given by the cyclic terms used in deriving the curve of Fig. 4; x: seasonally adjusted continuous analyzer bimonthly averages. The full curve is a plot of the cubic trend function used in deriving the curve of Fig. 4.

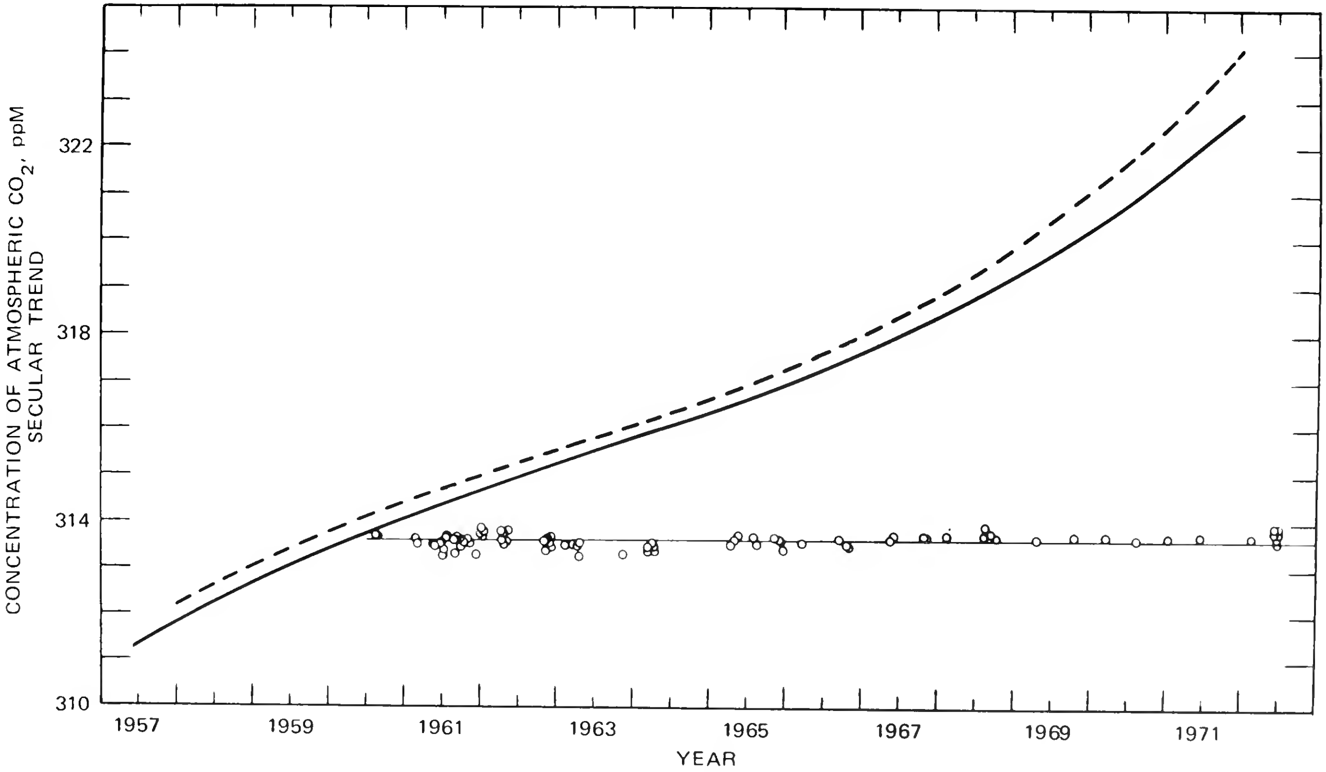

Fig. 6 Comparisons of secular trends of atmospheric CO_2 concentration at Mauna Loa and the South Pole. The dashed curve is for Mauna Loa; the full curve for the South Pole. ○: analyses of a Scripps Institution surveillance reference gas whose mean value is plotted as a straight line.

Since both trends were established on the basis of the same calibrating gases, the close agreement of results for each hemisphere does not prove the accuracy of the long-term increase in CO_2. Analysis of our principal surveillance gas (Fig. 6) indicates that the calibration has not significantly drifted, but analyses of additional surveillance gases suggest an upward drift, perhaps as much as 0.8 ppM. Since the secular increase is about 9 ppM, the atmospheric CO_2 variation may thus be underevaluated by as much as 10%. Manometric calibrations of reference gases, now in progress, should eventually establish a correction for any drift in the calibrating gases and reduce the relative uncertainty to about 5%. These calibrations will also better establish the absolute values of the reported mixing ratios.

From the average of the Hawaiian and South Pole trends, we estimate that the global average secular increase in the atmospheric concentration of CO_2 from 1959 to 1969 was 2.34% ± 0.20 of the presumed preindustrial value of 290 ppM. This is 49% of the industrial input as estimated by Keeling.[8] The relative uncertainty in this last figure is about 25% if we include the uncertainty in industrial input data.[8]

STRATEGY FOR INTERPRETING THE ATMOSPHERIC CO_2 RECORD

Owing to the complexity of the carbon cycle, real difficulties arise in devising a geochemical model to approximate its behavior. The model that we have formulated to interpret the new observational data on atmospheric CO_2 is more detailed than most of those used previously, and its properties are sufficiently complicated to deserve careful examination. As a preliminary test of these properties, we will now consider the two major classes of perturbations to which the carbon system can be subjected by a steadily working external carbon source. The first phenomenon, illustrated by the attenuation of cyclic ^{14}C variations, is essentially oscillatory in character, whereas the second, illustrated by the partitioning of industrial CO_2, is essentially exponential.

The mathematical transfer function which we derive to study the attenuation problem has the useful feature that it can afterward be modified to predict industrial CO_2 partitioning. An additional useful feature is that this function is analytical and relatively simple to evaluate, whereas the calculation of year-to-year predictions, considered later,[1] must be carried out by tedious numerical approximations of the governing equations. The two methods, one analytic and the other numerical, are essentially independent procedures, and, by requiring that they give concordant predictions, we reduce the risk of retaining computer programming blunders in our calculations.

SIGNIFICANCE OF RADIOCARBON VARIATIONS IN THE CARBON CYCLE

Since the oceans and the land biota both rapidly exchange CO_2 with the atmosphere and represent large reservoirs of carbon, knowledge of the fraction of industrial CO_2 remaining airborne is not sufficient information to determine the partitioning of CO_2 between the geochemical reservoirs. As several studies have shown,[9-11] we can learn more about that partitioning if we take into account the fractional dilution of atmospheric radiocarbon, $^{14}CO_2$, by inactive industrial CO_2 (the "Suess effect"). The distribution of ^{14}C in the deep-ocean water and estimates of atmospheric $^{14}CO_2$ before 1850 offer additional data to determine the quasi-steady-state preindustrial exchange rates of the carbon cycle.

Variations in ^{14}C from the beginning of the industrial era to 1954, when nuclear weapons testing added a new source of ^{14}C to the air, are known approximately from measurements of the radiocarbon/inactive carbon ratio, $^{14}C/C$, in wood samples dated by counting tree rings (Fig. 7). Before we attempt in the next paper[1] to deduce the Suess effect from this record, however, we will consider the question of whether or not the production of ^{14}C has varied significantly during the industrial era.

Previous studies of natural ^{14}C have reached conflicting conclusions as to whether the known variations in cosmic-ray flux can lead to significant fluctuations in ^{14}C abundance outside the stratosphere where ^{14}C is formed. The slow exchange of air between that reservoir and the lower atmosphere attenuates any such fluctuations, and further damping occurs when atmospheric $^{14}CO_2$ exchanges with the oceans and land biota. Although the magnitude of the stratospheric variation is uncertain, the degree of attenuation is the principal focus of controversy. This disagreement clearly results from the variety of geochemical models invented to predict the attenuation. We will now discuss this problem in some detail.

Stuiver[16] noted an inverse correlation between solar activity, as determined from sunspot records, and the ^{14}C concentration in modern wood. As shown in Fig. 8, the principal correlative feature is a ^{14}C peak and sunspot dip in the early 19th century. If the relation found by Stuiver holds for the period near 1950, the observed decrease in ^{14}C is partially due to a decrease in ^{14}C production. Taking the decrease solely as a measure of dilution of ^{14}C by industrial CO_2 will result in an overestimate of the industrial effect.

The physical explanation for Stuiver's discovery is believed to be that galactic primary cosmic rays (principally high-energy protons) which generate ^{14}C-producing neutrons in the stratosphere are more likely to be scattered out of the neighborhood of the earth's orbit during periods of increased solar activity. This enhanced scattering is probably due to increased turbulence in the solar wind along with alterations of the terrestrial magnetopause.

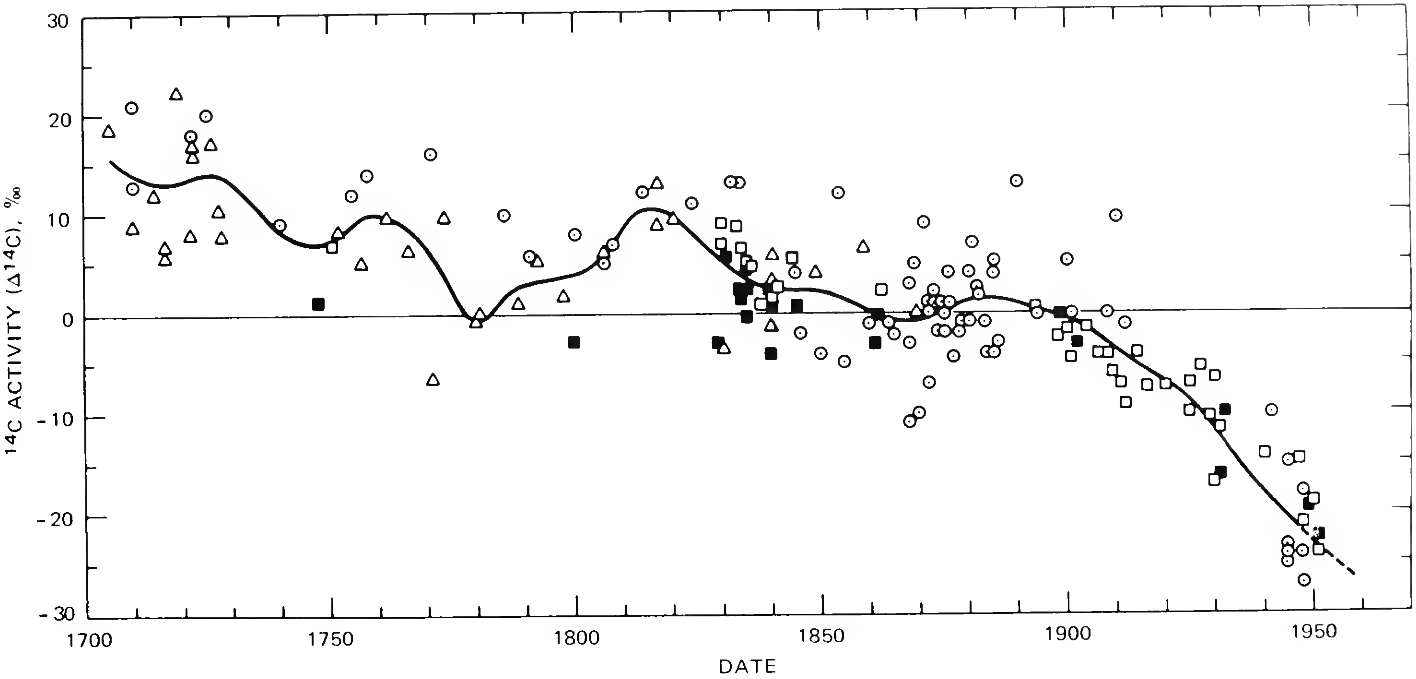

Fig. 7 ^{14}C content of tree-ring samples vs. their dates as determined by ring counts. The Δ^{14}C scale expresses the per mil deviation of the ^{14}C activity from an age-corrected oxalic acid standard. The full curve is drawn smoothly through averages of these data obtained for each period of solar activity. The sources of data (distinguished by different symbols) are: □, Lerman et al.,[12] Northern Hemisphere; ■, Lerman et al.,[12] Southern Hemisphere; ⊙, Suess,[13,14] Northern Hemisphere; △, Stuiver,[15] Northern Hemisphere.

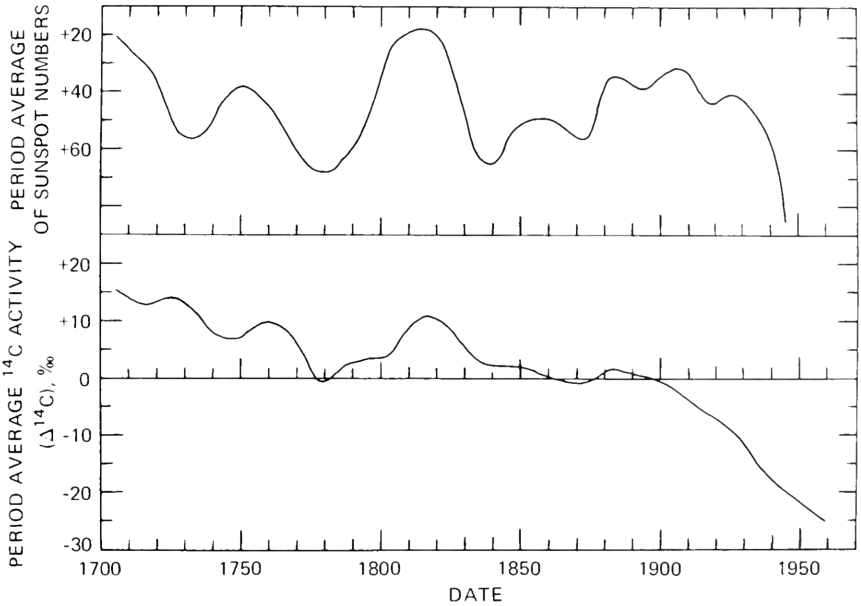

Fig. 8 Record of solar activity expressed by the sunspot numbers of Schove[17] compared with the ^{14}C content of wood samples dated by ring counts. Both records have been averaged over periods covering the intervals between solar minimums. The sunspot record has been inverted.

Furthermore, direct observations at recent solar-activity extremes indicate an inverse correlation of sunspot numbers and cosmic-ray intensity. From these data Lingenfelter[18] and Lingenfelter and Ramaty[19] have derived a linear relation between observed sunspot number and the global average ^{14}C production in the atmosphere on the basis of an analysis of the production of ^{14}C by cosmic rays. We attempt to establish in this and the succeeding paper how much such a modulation can interfere with estimates of the Suess effect.

Schove[17] observed that a fundamental 11-year cycle in sunspot activity is modulated by a slower cycle with a frequency of the order of 1/78 year^{-1}. A power spectrum of the sunspot (Wolf) numbers for the period 1700 to 1950 (Fig. 9) further reveals upper and lower modulation side bands at frequencies of approximately (1/11 ± 1/80) year^{-1} and (1/11 ± 2/80) year^{-1}. These are a general consequence of a nonlinear modulation of the higher frequency by the lower (actually centered at a period of about 85 years). Since the sunspot number returns to an almost constant value during years of minimum solar activity, the principal features of the sunspot record since 1700 are represented by the function (Fig. 10)

$$S(t) = C_1 + (C_2 + C_3 \sin 2\pi f_m t)(1 + \sin 2\pi f_0 t) \tag{1}$$

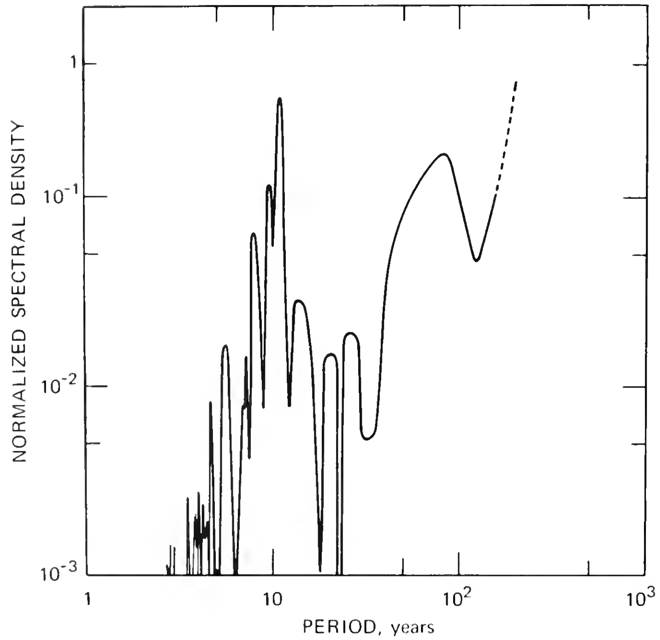

Fig. 9 Power spectrum of the sunspot record from 1700 to 1961, obtained from a discrete Fourier transform of the data record via the transform algorithm of Cooley and Tukey.[20] The transform terms were weighted to correspond to the Hann data window[21] and converted to a power spectrum. Two spectra, from the first and last 2^N data, were averaged in order to make use of all the data.

where $1/f_m \simeq 85$ years, $1/f_0 \simeq 11$ years, and C_1, C_2, and C_3 are constants (or vary only slightly over 85 years). Expanding this function gives

$$S(t) = C_1 + C_2 + C_2 \sin 2\pi f_0 t + C_3 \sin 2\pi f_m t$$
$$+ \frac{1}{2} C_3 [\cos 2\pi(f_0 - f_m)t - \cos 2\pi(f_0 + f_m)t] \qquad (2)$$

Because the final term in Eq. 2 contains frequencies close to 1/11 years, the long-period oscillation is well represented solely by the term $C_3 \sin 2\pi f_m t$, as would be the case if the 11-year cycle were ignored in Eq. 1. Thus in contradiction to the conclusion of Lal and Venkatavaradan,[22] the long-period cycle is properly treated as independent of the 11-year cycle when considering the attenuation of ^{14}C variations.

To determine whether or not these spectral components of the solar activity can seriously affect the ^{14}C record, we will first consider the simplest possible attenuating model, that of Grey and Damon,[23-25] in which a perturbation of the ^{14}C sources passes through a single atmospheric reservoir to a sink provided

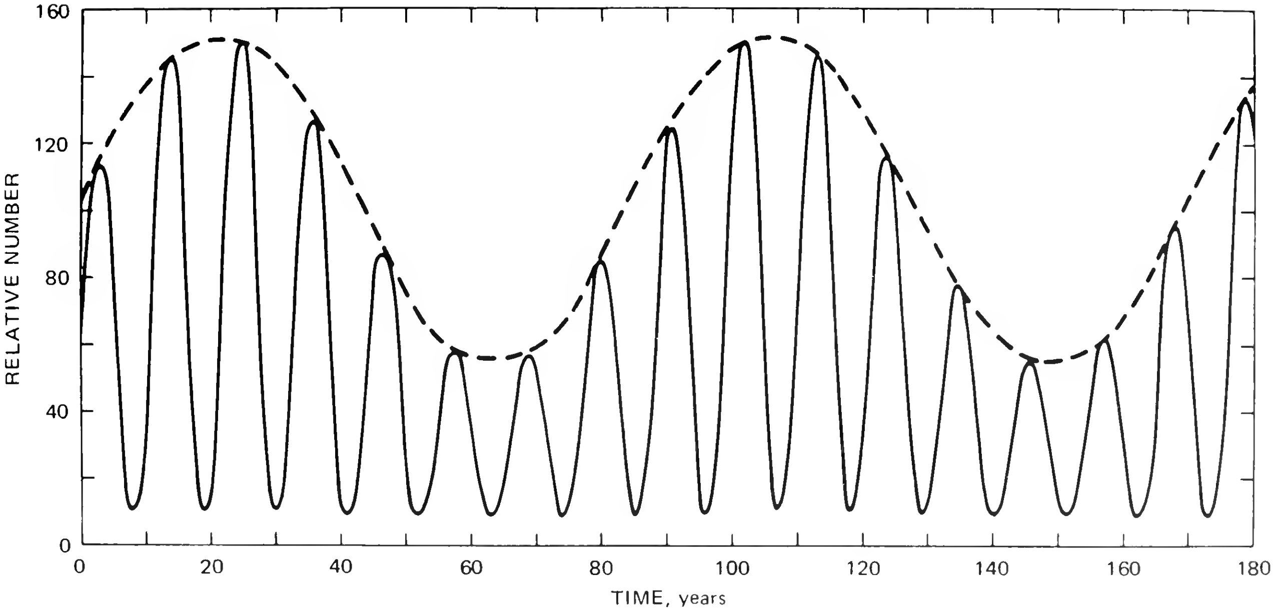

Fig. 10 Representation of the sunspot record given by Eq. 1 with the 85-year modulation shown as a dashed curve for emphasis. The parameters in Eq. 1 used for this graph were estimated from Schove's data.[17]

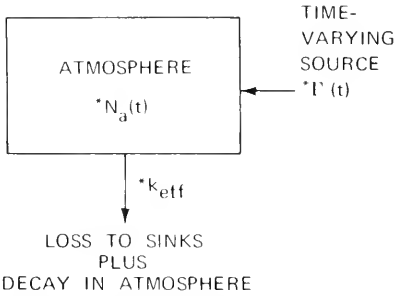

Fig. 11 Single reservoir model of atmospheric radiocarbon response to a time-varying source. The mass of atmospheric radiocarbon is $^*N_a(t)$; $^*k_{eff}$ is the effective net-transfer coefficient.

by adjacent reservoirs (Fig. 11). This model allows us to develop the mathematical approach of using a transfer function without requiring much analytical complexity.

The time-dependent mass of atmospheric ^{14}C, $^*N_a(t)$, produced by the variable ^{14}C source $^*\Gamma(t)$ is described by the equation

$$\frac{d^*N_a}{dt} = -{}^*k_{eff}{}^*N_a + {}^*\Gamma \tag{3}$$

where $^*\tau_{eff}$ ($\equiv {}^*k_{eff}^{-1}$) is the effective transfer time for the combined loss of ^{14}C by decay in the atmosphere and the net transfer to adjacent reservoirs. To solve Fig. 3, we decompose both the atmospheric ^{14}C mass and the source function into a steady-state term and a perturbation:

$$^*N_a(t) = {}^*N_{a0} + {}^*n_a(t) \tag{4}$$

$$^*\Gamma(t) = {}^*\Gamma_0 + {}^*\gamma(t) \tag{5}$$

yielding a steady-state equation

$$\frac{d^*N_{a0}}{dt} = 0 = -{}^*k_{eff}{}^*N_{a0} + {}^*\Gamma_0 \tag{6}$$

and a perturbation equation

$$\frac{d^*n_a}{dt} = -{}^*k_{eff}{}^*n_a + {}^*\gamma(t) \tag{7}$$

Grey and Damon,[25] using Lingenfelter's ^{14}C production equation and the observed annual sunspot record to establish $^*\gamma(t)$, approximately solved these

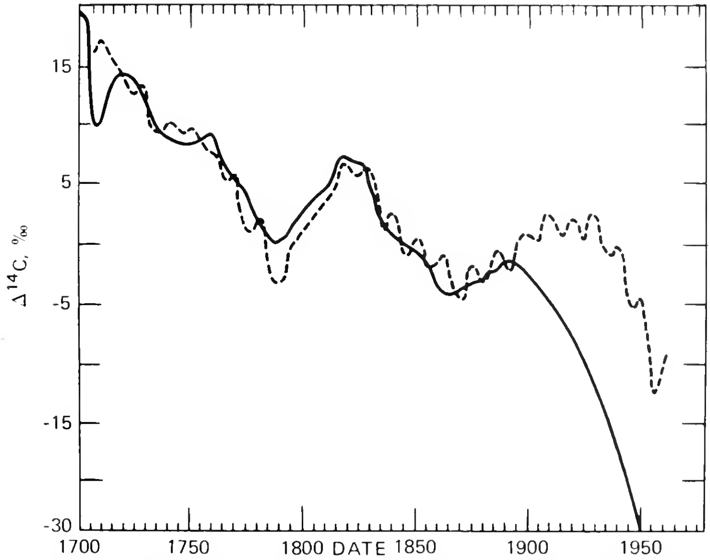

Fig. 12 Comparison of measured ^{14}C content ($\Delta^{14}C$) of tree rings (full curve) and that predicted by Grey and Damon[25] using a single reservoir model with an effective exchange time of $\tau_{eff} = 100$ years.

equations stepwise in 1-year increments to obtain a prediction of ^{14}C in the atmosphere. They varied the effective time constant, $^*\tau_{eff}$, and, for >40 years, obtained substantial agreement between the model prediction and the observed ^{14}C record for times prior to the 20th century, i.e., before dilution by inactive industrial CO_2 began to disturb the ^{14}C distribution significantly (Fig. 12). In spite of the apparently excellent prediction given by Grey and Damon's[25] model, there are objections to using such a simple model unless it can be shown that it actually approximates the behavior of atmospheric ^{14}C. Especially questionable is the use of a single adjustable time constant for which, as Grey states,[23] the correct value is "not immediately apparent from experimental observations."

To obtain a useful comparative index of the behavior of the one-parameter model, we will now express its basic properties in terms of a transfer-function ratio that describes, as a complex number, the attenuation and phase lag imposed on a sinusoidal variation in the ^{14}C production $^*\gamma(t)$ for any given oscillation frequency. This ratio may be derived either from the Fourier transform of Eq. 7 or more directly by setting the time-varying perturbations equal to complex harmonic variations:

$$^*\gamma(t) = {}^*\gamma(\omega)e^{i\omega t} \tag{8}$$

$$^*n_a(t) = {}^*n_a(\omega)e^{i\omega t} \tag{9}$$

where ω is the angular frequency, $i = \sqrt{-1}$, ${}^*\gamma(\omega)$ is the (time-invariant) amplitude of the oscillation in radiocarbon source at frequency ω, and ${}^*n_a(\omega)$ is a (time-invariant) complex factor that contains the amplitude and phase shift of the atmospheric ^{14}C variation, ${}^*n_a(t)$. Substituting Eqs. 8 and 9 in Eq. 7 and solving for ${}^*n_a(\omega)$ yields

$$ {}^*n_a(\omega) = (i\omega + {}^*k_{eff})^{-1}\, {}^*\gamma(\omega) \tag{10} $$

Dividing Eq. 10 by the steady-state solution (see Eq. 6)

$$ {}^*N_{ao} = \frac{{}^*\Gamma_0}{{}^*k_{eff}} \tag{11} $$

yields

$$ \frac{{}^*n_a(\omega)}{{}^*N_{ao}} = \left(\frac{{}^*k_{eff}}{i\omega + {}^*k_{eff}}\right) \frac{{}^*\gamma(\omega)}{{}^*\Gamma_0} \tag{12} $$

The transfer function we identify as

$$ Z_a(\omega) = (i\omega + {}^*k_{eff})^{-1} \tag{13} $$

The ratio

$$ \frac{Z_a(\omega)}{Z_a(0)} \equiv \left|\frac{Z_a(\omega)}{Z_a(0)}\right| e^{i\theta} = \frac{{}^*k_{eff}}{i\omega + {}^*k_{eff}} \tag{14} $$

relates, as a complex number, the fractional variations of the source to those of ^{14}C in the atmosphere. The attenuation at any frequency is given by the modulus

$$ \left|\frac{Z_a(\omega)}{Z_a(0)}\right| \equiv \frac{1}{\sqrt{1 + (\omega/{}^*k_{eff})^2}} \tag{15} $$

and the shift in phase by

$$ \theta(\omega) = -\tan^{-1}\left(\frac{\omega}{{}^*k_{eff}}\right) \tag{16} $$

If we evaluate Eqs. 15 and 16 with Grey and Damon's[25] preferred value of 100 years for ${}^*\tau_{eff}$, the 85-year component in the observed sunspot spectrum is predicted to appear in the atmosphere attenuated by a factor of 7.5 and the 11-year component by a factor of 57. As we will now show, these attenuations

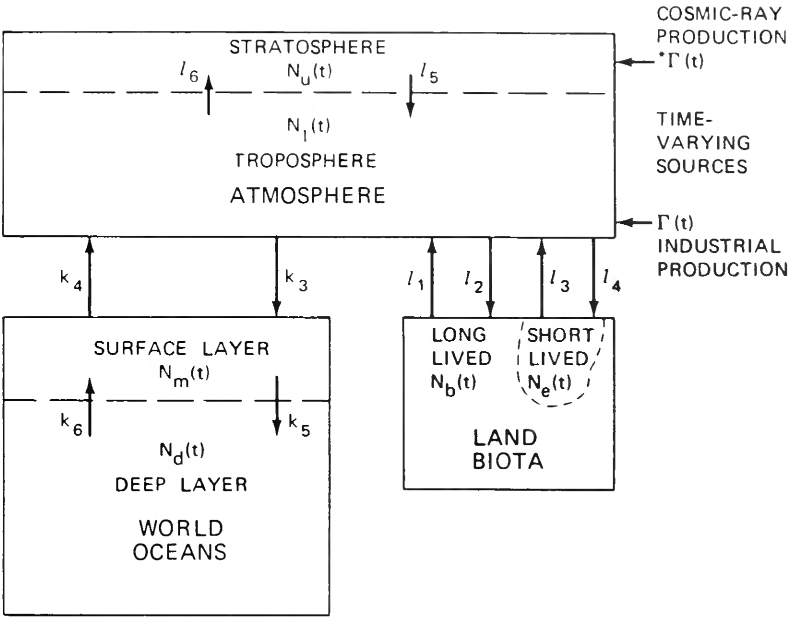

Fig. 13 Six-reservoir model of the carbon cycle. The mass of inactive carbon in each reservoir is represented by $N_j(t)$ (replaced by $*N_j(t)$ for radiocarbon), and the transfer coefficients between reservoirs are given by l_j and k_j (replaced by $*l_j$ and $*k_j$ for radiocarbon). In addition, the radiocarbon in each reservoir undergoes radioactive decay at the rate $*\lambda *N_j$.

are significantly less than predicted by models that take into fuller account the known properties of the natural carbon cycle.

For this demonstration we use a six-reservoir model (Fig. 13) that specifies the sinks for atmospheric $^{14}CO_2$ as the land biota, divided into long-lived and short-lived carbon pools, and the oceans, divided into surface and deep layers. Also, the lower atmosphere is distinguished from the stratosphere (where the ^{14}C source occurs), and carbon exchange is recognized to take place in both directions between all adjacent reservoirs. The justification for the division of the carbon cycle into these pools and pathways is discussed in greater detail in the next paper[1] and will not be duplicated here. The six-reservoir model, we note however, makes use of practically all available global observational data, and is clearly a more realistic attempt at modeling than the one-parameter model of Grey and Damon.[25]

The distribution of ^{14}C among the various reservoirs for the six-reservoir model is described by a set of six first-order (linear) differential equations, one for each reservoir. As with the one-reservoir model, we decompose the time-dependent mass of ^{14}C in each reservoir, $*N_j$, and the ^{14}C source term, $*\Gamma(t)$, into steady-state terms and the first-order time-varying perturbations, yielding a set of steady-state and time-dependent perturbation equations analogous to

TABLE 1

PARAMETERS FOR RESERVOIR MODELS

Five-Reservoir Model: Standard Case	
Transfer times	
*Atmosphere—surface ocean layer (air–sea)	τ_{am} = 6 years
*Deep ocean—surface ocean layer	τ_{dm} = 1500 years
Mass of inactive carbon in reservoirs	
*Surface ocean layer	$N_{mo} = 2.0\ N_{ao}$
†Total ocean	$N_{mo} + N_{do} = 63.0\ N_{ao}$
Short-lived land biota	$N_{eo} = 0.0459\ (N_{eo} + N_{bo})$
Long-lived land biota	$N_{bo} = 0.9541\ (N_{eo} + N_{bo})$
*Total land biota	$N_{eo} + N_{bo} = 2.65\ N_{ao}$
Atmosphere	$N_{ao} = 6.156 \times 10^{17}$ g
Inactive-carbon production rates for land biota	
Short-lived	$F_{eo} = 3.0 \times 10^{16}$ g year^{-1}
Long-lived	$F_{bo} = 2.6 \times 10^{16}$ g year^{-1}
Six-Reservoir Model: All Cases	
Transfer time	
Upper atmosphere—lower atmosphere	τ_{ul} = 2 years
Mass of inactive carbon in reservoirs	
Upper atmosphere (stratosphere)	$N_{uo} = 0.15\ N_{ao}$
Lower atmosphere (troposphere)	$N_{lo} = 0.85\ N_{ao}$

*Parameters were varied in nonstandard cases.

†For nonstandard cases this mass varies slightly to conform to the model equations given in Appendix C of the next paper (part II). (These equations assign constant values to the concentrations of carbon in the surface and deep-ocean layers and to the total volume of ocean water; the calculated value of N_{do} thus depends on the ratio N_{mo}/N_{ao} which may vary from case to case.)

Eqs. 4 and 5. We have verified that the system of equations for the six-reservoir model is mathematically stable for any set of positive transfer coefficients at any oscillation frequency. Also, we have determined that linearizing the governing transfer equations is justified because of the small relative variations in carbon distribution during the period of interest (prior to nuclear weapons testing). Accordingly (see Appendix A), we have derived for the six-reservoir model with an oscillating stratospheric source, the transfer-function ratio $Z_1(\omega)/Z_1(0)$, appropriate to the lower atmosphere, and obtained the attenuation and phase shift as a function of the frequency ω based on a representative set of model parameters (Table 1). For comparison we have also computed the attenuation and phase shift for the one-parameter model of Grey and Damon[25] and a five-reservoir

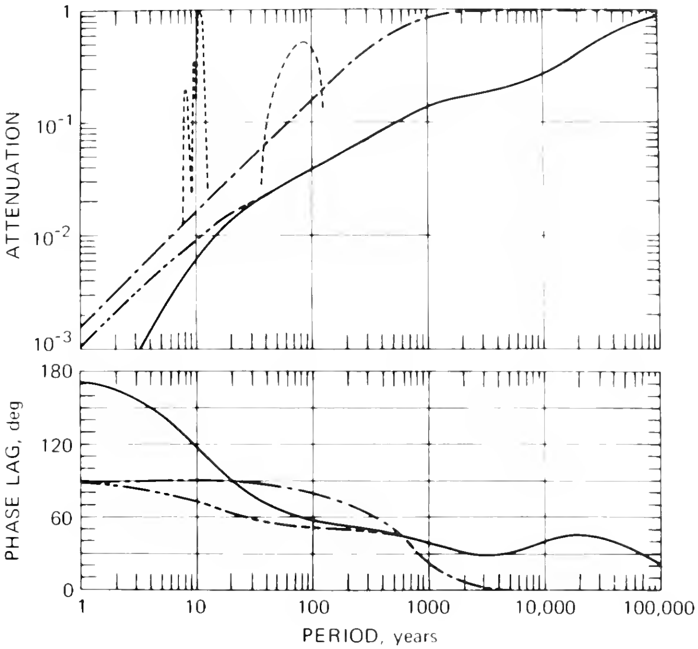

Fig. 14 Predicted attenuation and phase shift of ^{14}C in the lower atmosphere relative to an oscillating source in the upper atmosphere as a function of oscillation period. Predictions are given for three models: single reservoir model with τ_{eff} = 100 years (– · curve); five-reservoir model (–· · curve); six-reservoir model (full curve). Also shown (- - - curve) are the salient features of the 11- and 85-year bands in the sunspot spectrum. The five- and six-reservoir calculations are for the standard case given in Table 1.

model in which the stratosphere and lower atmosphere are not separated (Fig. 14). Except for the phase shift at high frequencies, the five- and six-reservoir cases differ only slightly. Both, however, predict attenuations roughly four times as great as those of Grey and Damon[25] at the frequencies of interest. These higher attenuations, already found for a series of two- and three-reservoir models by Houtermans,[26] significantly weaken the correlation between the predicted and observed atmospheric ^{14}C trend since 1700. The attenuation is sensitive principally to the parameters characterizing the air–sea interface. Even unrealistically large changes in the size of the land biota or the deep-ocean-to-surface-layer transfer time have little effect in the frequency range of interest (see Figs. 15 to 18). In no realistic case does a prediction approach that of the one-reservoir model. Unless the heliomagnetic ^{14}C variation is several times larger than assumed on the basis of Lingenfelter's[18] study of cosmic-ray data, the prediction of Grey and Damon[25] greatly exaggerates the variation in atmospheric $^{14}CO_2$ which can take place in direct correlation with sunspots.

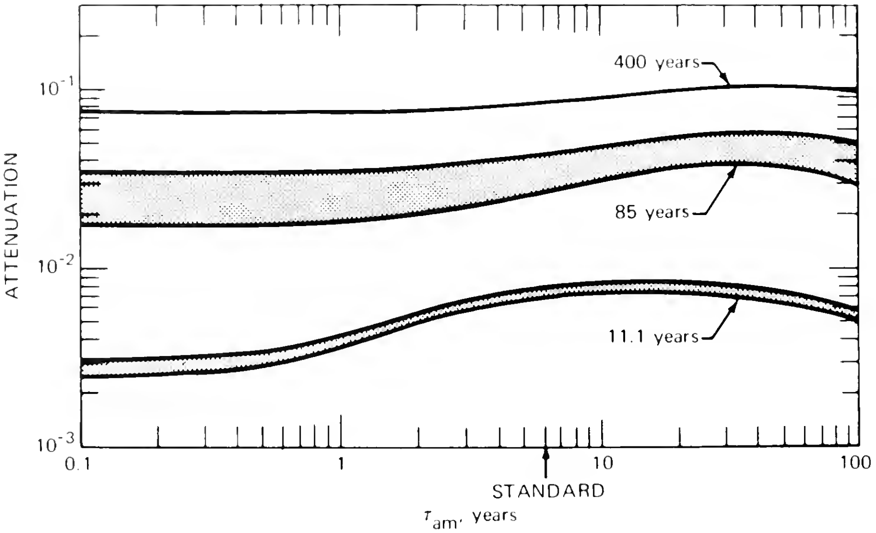

Fig. 15 Attenuation of 11- and 85-year bands (drawn at ½ peak height), vs. the atmosphere to ocean transfer time, τ_{am}. The value of τ_{am} used as a standard (6 years) is indicated by an arrow. A 400-year cycle, identified in tree-ring samples by Suess,[27] is shown as a reference.

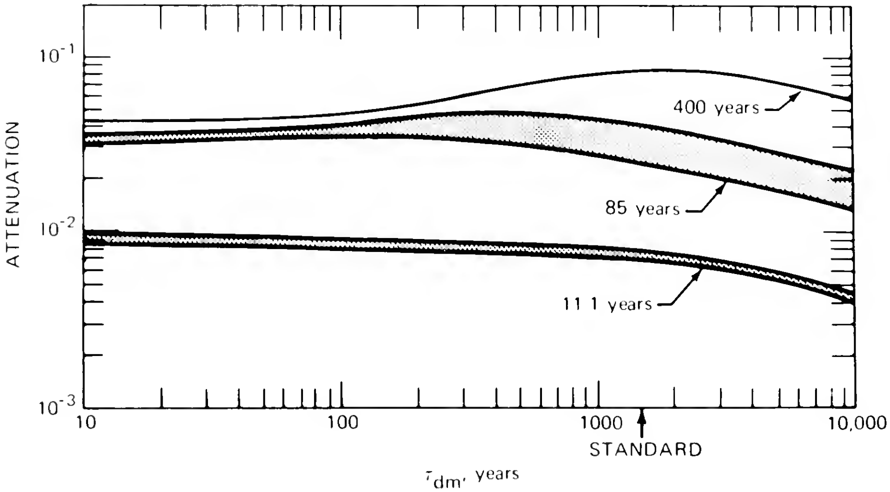

Fig. 16 Attenuation of 11- and 85-year bands, and a 400-year cycle, vs. the deep-ocean to surface-layer transfer time, τ_{dm}. The value of τ_{dm} used as the standard (1500 years) is indicated by an arrow.

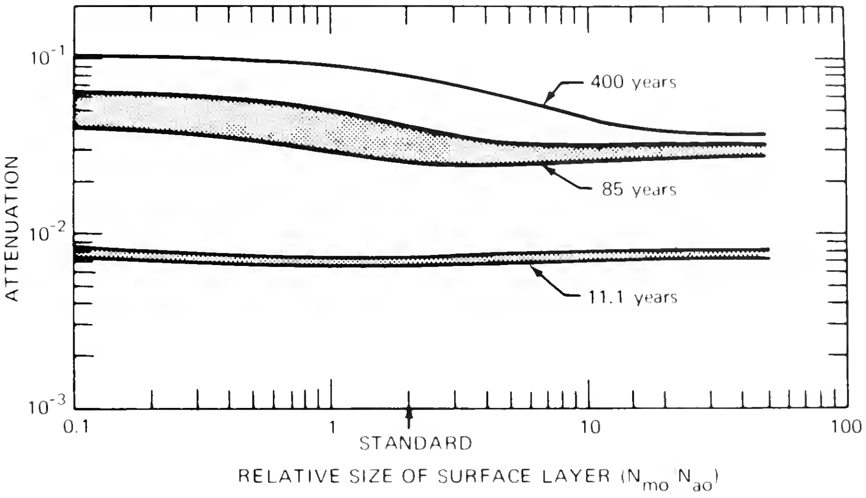

Fig. 17 Attenuation of 11- and 85-year bands, and a 400-year cycle, vs. the relative size of the ocean surface layer expressed in terms of the ocean surface layer to atmospheric carbon ratio, N_{m0}/N_{a0}. The size of N_{m0} used as a standard value ($2N_{a0}$) is indicated by an arrow.

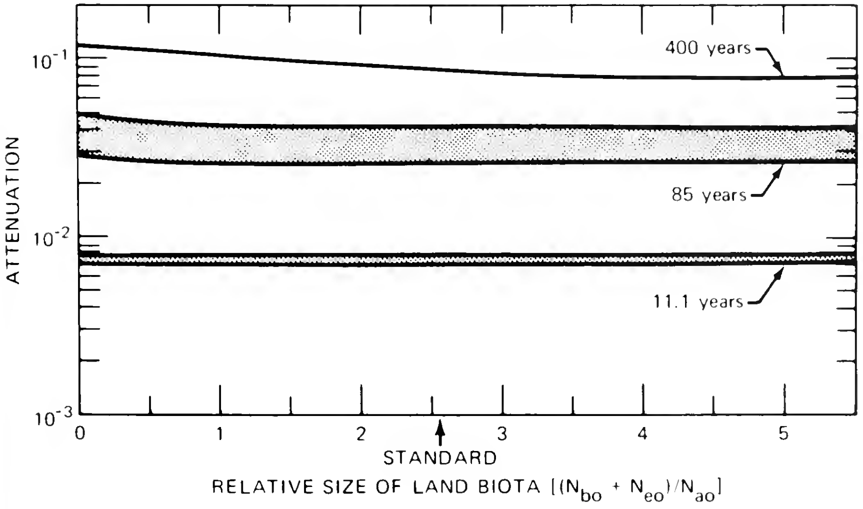

Fig. 18 Attenuation of 11- and 85-year bands, and a 400-year cycle, vs. the relative size of the land biota. The size used as the standard case ($N_{b0} + N_{e0} = 2.656\ N_{a0}$) is indicated by an arrow.

After looking closely at the ^{14}C observations (Fig. 7), and at the predictions given by the one-reservoir model (Fig. 12) and the six-reservoir model (Figs. 10 and 11 of the next paper[1]), we conclude that the tree-ring data for the period, 1700 to 1900, are not consistent enough to accept Stuiver's[15] correlation as thoroughly proven.

PARTITIONING OF INDUSTRIAL CO_2

The transfer function is of use not only in predicting the attenuation and phase shift of an oscillating source, but it also can be used to predict the redistribution of inactive CO_2 injected into the lower atmosphere by the burning of fossil fuels, if the rate of injection increases exponentially for a sufficient time that exponential increases establish themselves in all reservoirs of the system. By solving the system of model equations exactly, we have established that this requires only the order of 100 years. The transfer function thus leads to quite realistic results for current industrial CO_2 partitioning.

To illustrate this use of the transfer function, we shall again first consider the simple one-parameter model, in this case with a source term that is exponentially growing. The perturbation equation (Eq. 7) is applicable if we replace the oscillating source $^*\gamma$ with an exponential source of the form $\gamma(r)e^{rt}$. Dropping the asterisks so that the symbols in the equations now denote inactive carbon, we obtain, in place of Eq. 7,

$$\frac{dn_a}{dt} = -k_{eff}n_a + \gamma(r)e^{rt} \qquad (17)$$

where τ_{eff} ($\equiv k_{eff}^{-1}$) is the time constant for loss of inactive carbon to adjacent reservoirs, $\gamma(r)$ is a time-invariant factor, and $1/r$ is the time for an e-fold increase in the production rate. Assuming zero as the initial value of the perturbation, i.e.,

$$n_a(0) = 0$$

we integrate Eq. 17 to yield

$$n_a(t) = (r + k_{eff})^{-1}\gamma(r)(e^{rt} - e^{-k_{eff}t}) \qquad (18)$$

For continued exponential growth until $t \gg \tau_{eff}$, the second term in the last factor of Eq. 18 can be neglected. The perturbation grows in sympathy with the source but reduced by a factor that has the same form as the transfer function $Z_a(\omega)$ except that $i\omega$ is replaced by r, i.e.,

$$n_a(t) = Z_a(r)\gamma(r)e^{rt} \qquad (19)$$

where

$$Z_a(r) = (r + k_{eff})^{-1} \tag{20}$$

To obtain the instantaneous partitioning (i.e., the rate of accumulation of CO_2 in the atmosphere divided by the rate of industrial production), we differentiate Eq. 19. This leads to

$$\frac{dn_a/dt}{\gamma(r)e^{rt}} = rZ_a(r) \tag{21}$$

To obtain the total partitioning, i.e., the mass of industrial CO_2 that has accumulated in the atmosphere during the industrial era divided by the total production of industrial CO_2, M, we first divide Eq. 19 by

$$M = \int_0^t \gamma(r)e^{ru}du = r^{-1}\gamma(r)(e^{rt} - 1) \simeq r^{-1}\gamma(r)e^{rt} \tag{22}$$

where u is a "dummy" variable of integration. For times substantially greater than 1/r, the latter equality holds approximately, and

$$\frac{n_a(t)}{M} = rZ_a(r) \tag{23}$$

i.e., for times long compared to both 1/r and τ_{eff}, the instantaneous and total partitioning approach the same value.

To investigate the importance of the various model parameters in determining the long-term partitioning of industrial carbon in the cycle, we have derived atmospheric transfer functions for five- and six-reservoir models with an exponentially growing atmospheric source (Appendix B). A value of 1/22 years^{-1} was chosen for the exponential factor, r, to reflect the average rate of increase in industrial CO_2 production during the past decades.

The fraction of inactive industrial CO_2 remaining in the lower atmosphere (Figs. 19 to 21) is somewhat more sensitive to variations in the transfers within the oceans than was the attenuation of oscillations in the ^{14}C production rate in the same reservoir. The fraction also depends on possible increase in carbon of the land biota (Fig. 22), a change not significant in the ^{14}C model calculations. (The possible growth of the land biota is parameterized in the model by a growth factor, β, such that if the concentration of atmospheric CO_2 increases by x%, the rate of assimilation of CO_2 increases by βx% per unit mass of land plants.) Of special interest is that the inclusion or neglect of the stratosphere as a separate reservoir has very little influence on the partitioning of industrial CO_2 (Fig. 23). For realistic values of the oceanic transfer coefficients and reservoir sizes, the fraction remaining in the lower atmosphere agrees with our current

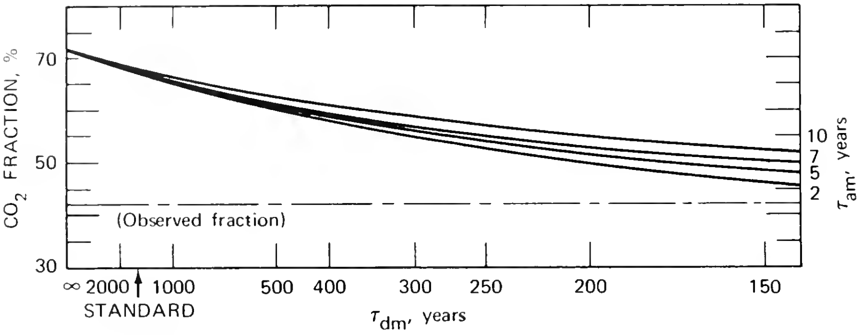

Fig. 19 Fraction of industrial CO_2 remaining in the lower atmosphere as a function of the deep-ocean-to-surface-layer transfer time, τ_{dm}, for several values of the (total) atmosphere to ocean transfer time τ_{am}. The average fraction observed for the lower atmosphere between 1959 to 1969 (42%) is indicated by a horizontal line, and the value of τ_{dm} used as a standard case (1500 years) is indicated by an arrow.

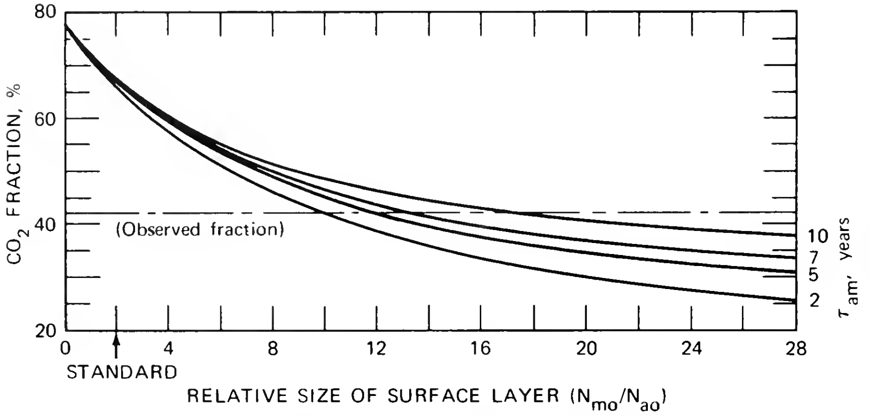

Fig. 20 Fraction of industrial CO_2 remaining in lower atmosphere as a function of the relative size of the ocean surface layer, for several values of the atmosphere to ocean transfer time, τ_{am}. The average fraction observed from 1959 to 1969 (42%) is indicated by a horizontal line, and the value of N_{m0} used as a standard case ($2N_{a0}$) is indicated by an arrow.

estimate of 49% for the entire atmosphere and hence 42% for the lower atmosphere only if the land biota increases in size.

The use of the transfer function is not intended to achieve precise predictions. Its principal value is to permit a rapid survey of how the attenuation and partitioning predicted by a linear model vary with assumed values of the model parameters. The function also offers a control to check the computational accuracy of time-dependent predictions which involve numerical approximations. In the paper that follows (part II), the time-dependent governing equations of the six-reservoir model will be used in conjunction with the actual

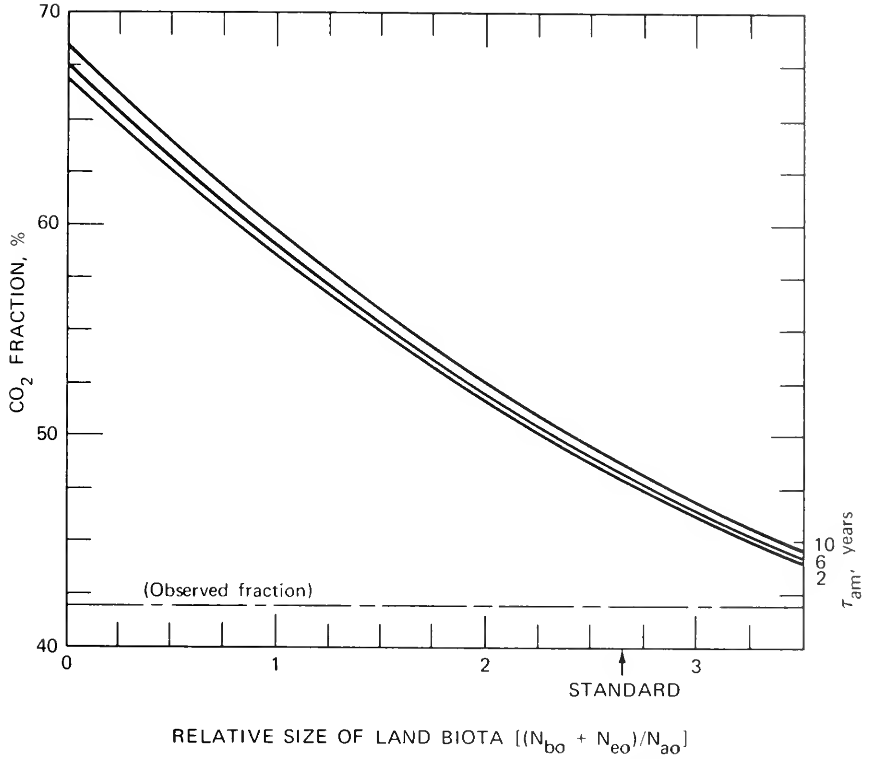

Fig. 21 Fraction of industrial CO_2 remaining in the lower atmosphere as a function of the relative size of the land biota, for several values of the atmosphere to ocean transfer time, τ_{am}, and a biota growth factor of 0.25. The average fraction observed from 1959 to 1969 (42%) is indicated by a horizontal line, and the size of the biota used as a standard case ($N_{b_0} + N_{e_0} = 2.656\ N_{a_0}$) is indicated by an arrow.

records of industrial production and sunspot numbers to examine in greater detail the properties of the natural carbon cycle and to make time-dependent predictions.

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We thank Paul Damon, Johann Vogel, George M. Woodwell, and Hans Suess for advice regarding the land biota and radiocarbon, and Peter Guenther and Alex Adams for help in carrying out the computations. The authors are also indebted to Anne Thistle for special help in preparing the typescript. Support was given by the Atmospheric Sciences Division of the National Science Foundation under Grant GA-31324X.

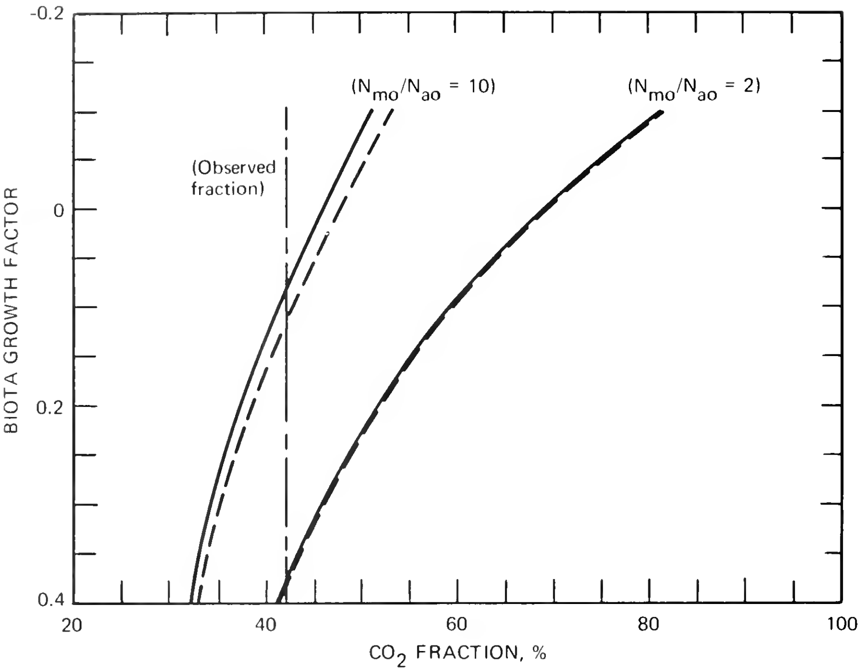

Fig. 22 Biota growth factor vs. fraction of industrial CO_2 remaining in the lower atmosphere, for various atmosphere-to-ocean transfer times and ocean-surface-layer sizes. The observed fraction in 1970 (42%) is indicated by a vertical line in this figure. Atmosphere-to-ocean transfer time: —, 5 years; - - - -, 7 years.

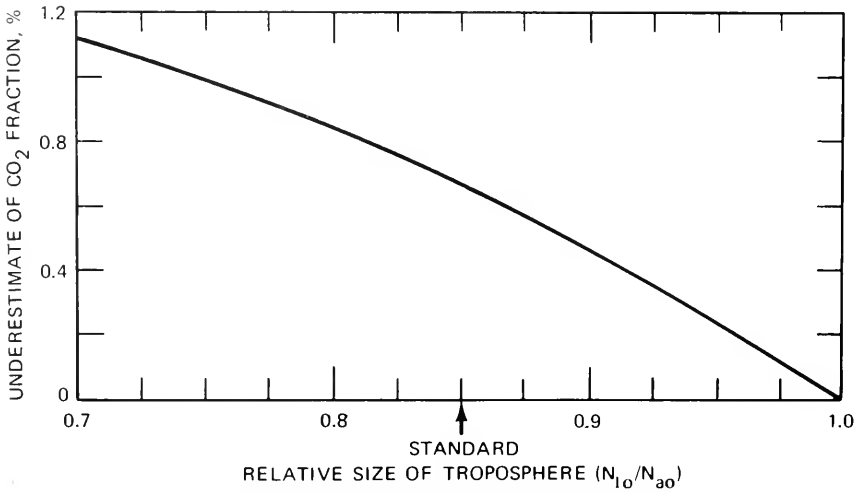

Fig. 23 The underestimate of the fraction of industrial CO_2 remaining in the lower atmosphere (troposphere) owing to neglect of the finite transfer time between the upper and lower atmospheres.

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DISCUSSION BY ATTENDEES

Allen: Dr. Ekdahl, you ended your presentation with the comment that we need to know more about the effect of the increase in atmospheric CO_2 on the biota. I will comment briefly on the effects of CO_2 concentration on a short-term basis on plants. Dr. Lemon's project at Ithaca, N. Y., has developed a computer model of the soil–plant–atmosphere (SPAM) which can be used to predict the effects of increased CO_2 concentration on plant-community photosynthesis. The most critical parameter in this model is the response of leaf stomata to CO_2 concentration. Many terrestrial higher plants open their stomata in response to light. Of these types of plants, some partially close their stomata in response to higher than normal CO_2 concentration and others do not respond very much to external CO_2 concentration. When the atmospheric CO_2 concentration was increased by 27% (from 315 ppM to 400 ppM), there was an increase of 7 to 9% in net photosynthesis using the partial stomatal closure model. Simulations of plants that do not close stomata in response to CO_2 gave a 21% increase. Furthermore, increases in diffuse radiation which may accompany climatic changes often gave larger predicted net photosynthesis rates. In general, with 30% of total solar radiation coming from a diffuse hemispherical source, predicted net photosynthesis rates were higher than with 10% diffuse radiation even though total solar radiation was about 25% less.

APPENDIX A: CALCULATION OF TRANSFER FUNCTIONS FOR ATTENUATION OF RADIOCARBON SOURCE OSCILLATIONS

Transfer functions for the five- and six-reservoir models may be determined in much the same manner as was employed for the one-reservoir model described in the text. Each of the $^*N_j$, denoting the mass of ^{14}C in each reservoir j, is decomposed into steady-state and perturbation terms, as is the stratospheric ^{14}C source term, $^*\Gamma$:

$$^*N_j = {}^*N_{j0} + {}^*n_j(t), \qquad j = 1, 2, \ldots, 5 \text{ or } 6 \tag{A.1}$$

$$^*\Gamma = {}^*\Gamma_0 + {}^*\gamma(t) \tag{A.2}$$

Substitution of Eqs. A.1 and A.2 into the governing equations (see Appendix A of part II) yields a decomposition into a set of steady-state equations:

$$\frac{d^*N_{j0}}{dt} = 0 = \sum_{\substack{j'=1 \\ j' \neq j}} ({}^*k_{j'j}{}^*N_{j'0} - {}^*k_{jj'}{}^*N_{j0}) - {}^*\lambda{}^*N_{j0} + {}^*\Gamma_{j0} \tag{A.3}$$

and a set of perturbation equations

$$\frac{d^*n_j}{dt} = \sum_{\substack{j'=1 \\ j' \neq j}} ({}^*k_{j'j}{}^*n_{j'} - {}^*k_{jj'}{}^*n_j) - {}^*\lambda{}^*n_j + {}^*\gamma_j \tag{A.4}$$

where the $^*k_{jj'}$ and $^*k_{j'j}$ are transfer coefficients, $^*\lambda$ is the ^{14}C decay constant (= 1/8267 years), and the source terms are nonzero only for the stratosphere.

Again, harmonic variations are assumed for the ^{14}C mass and source perturbations:

$$^*n_j(t) = {}^*n_j(\omega)e^{i\omega t} \tag{A.5}$$

$$^*\gamma(t) = {}^*\gamma(\omega)e^{i\omega t} \tag{A.6}$$

and the resulting linear algebraic equations are solved simultaneously for the variables $^*n_j(\omega)$. In the five-reservoir model, the atmospheric transfer function, $Z_a(\omega)$, is computed as the ratio of two determinants

$$^*Z_a(\omega) = {}^*\nu_a(U)/{}^*D_5(U) \tag{A.7}$$

where $U = i\omega + {}^*\lambda$. The term ${}^*\lambda$ comes into the expression for ${}^*Z_a(\omega)$ as a result of the terms ${}^*\lambda{}^*n_j$ in Eq. A.4. In the six-reservoir model, the lower atmospheric (troposphere) transfer function is written

$$ {}^*Z_l(\omega) = {}^*\nu_1(U)/{}^*D_6(U) \tag{A.8} $$

The coefficients of the ${}^*n_j$ and ${}^*n_{j'}$ in Eq. A.4 form a square array (matrix) of elements. These elements are identically the elements of a determinant which, for the six-reservoir case, is

$$ {}^*D_6(U) = \begin{vmatrix} U + {}^*l_5 & 0 & 0 & -{}^*l_6 & 0 & 0 \\ 0 & U + {}^*l_3 & 0 & -{}^*l_4 & 0 & 0 \\ 0 & 0 & U + {}^*l_1 & -{}^*l_2 & 0 & 0 \\ -{}^*l_5 & -{}^*l_3 & -{}^*l_1 & U + {}^*k_3 + {}^*l_2 + {}^*l_4 + {}^*l_6 & -{}^*k_4 & 0 \\ 0 & 0 & 0 & -{}^*k_3 & U + {}^*k_4 + {}^*k_5 & -{}^*k_6 \\ 0 & 0 & 0 & 0 & -{}^*k_5 & U + {}^*k_6 \end{vmatrix} \tag{A.9} $$

In place of the transfer coefficients, ${}^*k_{jj'}$, of Eq.'s A.3 and A.4, we have here written ${}^*l_i$ and ${}^*k_i$ to coincide with the notation of Keeling[28] and that of the next paper where explicit expressions are given. For the five-reservoir case, ${}^*D_5(U)$ is obtained from Eq. A.9 by setting ${}^*l_6 = 0$ in the 5 by 5 principal minor of $U + {}^*l_5$. Explicit algebraic expressions are

$$ {}^*D_5(U) = (U^4 + {}^*AU^3 + {}^*BU^2 + {}^*CU + {}^*D)U \tag{A.10} $$

$$ {}^*D_6(U) = (U + {}^*l_5){}^*D_5(U) + {}^*l_6(U + {}^*l_3)(U + {}^*l_1)(U^2 + {}^*aU + {}^*b)U \tag{A.11} $$

where

$$ \left. \begin{aligned} {}^*A &= \sum_{j=1}^{4} {}^*l_j + \sum_{j=3}^{6} {}^*k_j \\ {}^*B &= ({}^*l_1 + {}^*l_3)({}^*k_3 + {}^*k_4 + {}^*k_5 + {}^*k_6) \\ &\quad + ({}^*l_2 + {}^*l_4)({}^*k_4 + {}^*k_5 + {}^*k_6) + {}^*k_3({}^*k_5 + {}^*k_6) + {}^*k_4{}^*k_6 \\ &\quad + {}^*l_1{}^*l_3 + {}^*l_1{}^*l_4 + {}^*l_2{}^*l_3 \\ {}^*C &= ({}^*l_1 + {}^*l_3)({}^*k_3{}^*k_5 + {}^*k_3{}^*k_6 + {}^*k_4{}^*k_6) + ({}^*l_2 + {}^*l_4)({}^*k_4{}^*k_6) \\ &\quad + {}^*l_1{}^*l_3({}^*k_3 + {}^*k_4 + {}^*k_5 + {}^*k_6) \\ &\quad + ({}^*l_1{}^*l_4 + {}^*l_2{}^*l_3)({}^*k_4 + {}^*k_5 + {}^*k_6) \\ {}^*D &= {}^*l_1{}^*l_3({}^*k_3{}^*k_5 + {}^*k_3{}^*k_6 + {}^*k_4{}^*k_6) + ({}^*l_1{}^*l_4 + {}^*l_2{}^*l_3){}^*k_4{}^*k_6 \end{aligned} \right\} \tag{A.12} $$

$$\left.\begin{aligned} {}^*a &= {}^*k_4 + {}^*k_5 + {}^*k_6 \\ {}^*b &= {}^*k_4 {}^*k_6 \end{aligned}\right\} \tag{A.13}$$

The numerators of $^*Z_a(\omega)$ and $^*Z_l(\omega)$ are given by the expressions

$$^*\nu_a(U) = (U + {}^*l_3)(U + {}^*l_1)(U^2 + {}^*aU + {}^*b) \tag{A.14}$$

$$^*\nu_l(U) = {}^*l_5(U + {}^*l_3)(U + {}^*l_1)(U^2 + {}^*aU + {}^*b) \tag{A.15}$$

The transfer functions evaluated at zero angular frequency are obtained by setting $\omega = 0$, i.e., $U = {}^*\lambda$ in $Z_a(\omega)$ and $Z_l(\omega)$, and the fractional response in the designated reservoir to a fractional perturbation in the source is given (for the five- and six-reservoir cases, respectively) by

$$\frac{^*n_a(\omega)}{^*N_{a0}} = \frac{Z_a(\omega)}{Z_a(0)} \cdot \frac{^*\gamma(\omega)}{^*\Gamma_0} \tag{A.16}$$

$$\frac{^*n_l(\omega)}{^*N_{l0}} = \frac{Z_l(\omega)}{Z_l(0)} \cdot \frac{^*\gamma(\omega)}{^*\Gamma_0} \tag{A.17}$$

analogous to the one-reservoir model (Eq. 12).

APPENDIX B: TRANSFER FUNCTIONS FOR PARTITIONING OF INDUSTRIAL CO_2

The perturbation of inactive carbon in each reservoir, n_j, owing to the injection of fossil fuel into the lower atmosphere, is described by an equation analogous to Eq. A.4, i.e.,

$$\frac{dn_j}{dt} = \sum_{\substack{j'=1 \\ j' \neq j}} (k_{j'j} n_{j'} - k_{jj'} n_j) + \gamma_j(t), \qquad j = 1, 2, \ldots, 5 \text{ or } 6 \tag{B.1}$$

where the source terms $\gamma_j(t)$ are zero for all except the lower atmospheric reservoir. For an exponentially growing source

$$\gamma(t) = \gamma(r)e^{rt} \tag{B.2}$$

the exact solution to Eq. B.1 is expressed as a sum of terms that decay exponentially plus one that grows in sympathy with the source:

$$n_j(t) = \sum_{j'=1} C_{jj'} e^{-\lambda_{j'} t} + Z_j(r)\gamma(r)e^{rt} \tag{B.3}$$

where the $C_{jj'}$ are constants (functions of the $k_{jj'}$), and the factors $\lambda_{j'}$ are nonnegative roots (eigenvalues) of the characteristic determinant Eq. A.9 except that transfer coefficients, k_i and l_i, appropriate to the inactive carbon, replace the $^*k_i$ and $^*l_i$, and U is set equal to r. For times long compared to the longest of the characteristic time constants, $\lambda_{j'}^{-1}$, the last, exponentially growing term dominates, and, as was found for the one-reservoir case, the partitioning is proportional to the transfer function, $Z_j(r)$. For the six-reservoir model, the lower atmosphere (tropospheric) transfer function is

$$Z_1(r) = \frac{\nu_1(r)}{D_6(r)} \tag{B.4}$$

where

$$D_6(r) = r[(r + l_5)(r^4 + Ar^3 + Br^2 + Cr + D) + l_6(r + l_3)(r + l_1)(r^2 + ar + b)] \tag{B.5}$$

and

$$\nu_1(r) = (r + l_5)(r + l_3)(r + l_1)(r^2 + ar + b) \tag{B.6}$$

The coefficients A, B, C, D, and a and b are the same functions of the (unstarred) transfer coefficients as are their starred counterparts listed in Eqs. A.12 and A.13. The transfer coefficients l_i and k_i for the inactive carbon system are listed in Appendix C of part II with the exception that here, in order to simplify the matrix (Eq. A.9), we set $l_7 = 0$. This is equivalent to assuming that the short-lived biota is governed by a transfer equation of exactly the same form as for the long-lived biota, i.e., each reservoir assimilates CO_2 at a rate proportional to its own mass. The effect is a reduction of the magnitude of the biota growth factor, β for a given uptake of industrial CO_2 by the biota as a whole, but there is otherwise little influence on the predictions described here.

For the five-reservoir model [which has the source $\gamma(t)$ appearing in the same reservoir as for the radiocarbon case],

$$Z_a(r) = \frac{\nu_a(r)}{D_5(r)} \tag{B.7}$$

where $\nu_a(r)$ and $D_5(r)$ are of the same form as Eqs. A.14 and A.10. The instantaneous and total partitionings for an exponential industrial CO_2 source are equal to $rZ_1(r)$ for the six-reservoir model, and $rZ_a(r)$ for the five-reservoir model.

Finally, since the perturbation in each reservoir grows in sympathy with the source after lapse times long enough that a calculation using Z(r) is valid, a direct method of extracting the partitioning in all reservoirs is to substitute

$$n_j(t) = Z_j(r)e^{rt} \qquad \text{(B.8)}$$

directly into the B.1 equations, cancel out the common factor of e^{rt} in each equation, and then solve simultaneously the resulting algebraic linear equations for the various $Z_j(r)$. This method is algebraically equivalent to the harmonic analysis used to form the $^*Z_j(\omega)$ and indeed employs the same fundamentally more general Fourier or Laplace transforms of the n_j and $^*n_j$, as discussed by Keeling.[28]

Our present method of analyzing reservoir models has the simplicity that the roots of the determinantal equations D(U) = 0 need not be found explicitly. It must be known, however, that they are all real positive numbers (one may be zero) before the transfer functions can be proved to lead to stable results over long time periods. This has been verified for all cases presented in this paper.

ATMOSPHERIC CARBON DIOXIDE AND RADIOCARBON IN THE NATURAL CARBON CYCLE: II. CHANGES FROM A. D. 1700 TO 2070 AS DEDUCED FROM A GEOCHEMICAL MODEL

ROBERT BACASTOW and CHARLES D. KEELING
Scripps Institution of Oceanography, University of California at San Diego,
La Jolla, California

ABSTRACT

A nonlinear geochemical model of the interaction of atmospheric CO_2 with the oceans and land biota has been constructed to predict future changes in atmospheric CO_2 concentration in the next century. If production of CO_2 from fossil fuels continues, the perturbations from preindustrial times may become so large that a linear model is unrealistic, especially because it fails to take into account that ocean surface water will become progressively more acid and less able to absorb each new increment of industrial CO_2. On the assumption that industrial CO_2 production continues to increase at the rate of the past 20 years and that the ultimate increase in biomass of the land biota is no more than twice the present biomass, the atmospheric CO_2 concentration will reach a value six to eight times the preindustrial value in 100 years.

When the radiocarbon concentration in dated wood and the recent atmospheric increase in CO_2 are compared in the context of the model, it appears that the land biomass has increased 1 to 3% since the beginning of the industrial era. This calculation takes account of the actual year to year variations in industrial CO_2 production and the heliomagnetic variation in radiocarbon production in the stratosphere. The inferred biomass increase, presumably owing to CO_2 fertilization, is too small to be verified by direct observation and is not considered to be established. On the other hand, the trend in atmospheric CO_2 apparently rules out any large recent change in biomass.

Combustion of fossil fuels (coal, petroleum, and natural gas) is adding increasing amounts of carbon dioxide (CO_2) to the atmosphere each year. The fate of this CO_2 attracts interest because a sustained increase might modify the earth's climate through the "greenhouse" effect[1] and because, from the effects of this input, we may learn more about the earth's carbon cycle.

We have constructed a geochemical model of the natural reservoirs into which industrial CO_2 can mix. Our first objective is to predict the CO_2 concentration in the atmosphere during the next century, when atmospheric

CO_2 may be several times as abundant as at present. As a second objective, we wish to determine separately the fractions of industrial CO_2 taken up by the oceans and the land biota. For our purposes, the land biota is meant to include all land and freshwater plants and their detritus. Its mass on a dry-weight basis we will call the "land biomass."

To obtain a realistic model of CO_2 air–sea exchange, we find we must include a nonlinear effect related to acidification of the surface layers of the world's oceans. This effect has not been included in previous models. Deep-ocean water has a large capacity for storing CO_2, and most industrial CO_2 will eventually reside there or in the sediments below. The surface water serves as a barrier, however, and, as it absorbs CO_2, it becomes more acidic and even more of a barrier.

Direct measurements of CO_2 in the atmosphere and of the radioactive isotope ^{14}C in dated wood and in ocean water help fix parameters in the model. It turns out that the model predictions agree with observations only if the land biota has recently increased in mass. If correct, this finding is significant because direct measurements of communities of land plants are inadequate to determine worldwide trends in biomass and are even inadequate to determine whether the biomass has increased or shrunk in recent years.

RESERVOIR EXCHANGE MODEL FOR CO_2

The pools and pathways of the natural carbon cycle are complex and only partially documented; investigators, when formulating mathematical models, are forced to make simplifying assumptions. Some simplifications are readily acceptable on geochemical grounds; for example, modelists usually consider it safe to ignore such inorganic solid-phase reactions as rock weathering and limestone formation when considering short-term atmospheric perturbations because such reactions are relatively slow. Other simplifications are made to reduce mathematical complexity. For example, if the governing equations for interacting carbon pools are solved by analytical techniques, the number of reservoirs that can be considered at one time is limited by how many simultaneous first-order differential equations the modelist is willing to solve. First-order exchange processes are usually assumed so that the equations are linear.

Using an analytical approach in modeling industrial CO_2 perturbations, Revelle and Suess[2] considered the spatially averaged atmosphere and world oceans as two reservoirs; Bolin and Eriksson[3] modified this model by dividing the oceans into surface and deep water. Plesset and Dugas,[4] including the humus as a fourth reservoir, calculated the decay of excess ^{14}C from nuclear explosions. Keeling[5] worked out the solution of a five-reservoir model with two land-biota reservoirs, and Plesset and Latter[6] worked out the solution of a similar six-reservoir model with the atmosphere divided into the stratosphere and troposphere. In the preceding paper, Ekdahl and Keeling show part of the solution for a six-reservoir model involving both inactive carbon and radiocarbon. This latter model obviously taxes one's patience: to solve it completely requires that 36 fifth-order determinants be worked out in addition to finding the roots of two quintic equations.

During the past decade, numerical approximation methods have been used more and more frequently to solve problems involving perturbations in the carbon cycle. In most cases the modelists prescribe annual steps in a perturbing source and then, by digital computer, calculate successive redistributions within the carbon pools. The short-term influence of industrial CO_2 in the atmosphere, oceans, and biota has been considered in this way by Broecker, Li, and Peng,[8] and by Machta.[9] By similar means Baxter and Walton[10] have predicted the dilution of radiocarbon by industrial CO_2. All these investigators retained linear features of the earlier analytic models, even though more precise nonlinear expressions could have been used.

In one of the earliest but most interesting models of the carbon cycle, Eriksson and Welander[11] considered nonlinear interactions between the atmosphere, biota, and oceans. They numerically solved the complex governing equations using a digital computer. No subsequent investigator has imitated their technique.

Our model portrays the natural reservoirs of the short-term carbon cycle in the configuration shown in Fig. 1. The atmosphere, for some calculations, is divided into an upper layer, the stratosphere, and a lower layer, the troposphere. The land biota is split into two partially coextensive reservoirs. The long-lived biota (with an average carbon transfer time of 60 years) models wood and humus. The short-lived biota (average transfer time 2½ years) models annual plants, leaves, and short-lived detritus. Both exchange carbon directly with the atmosphere. The deep ocean, comprising the bulk of the ocean water, exchanges carbon with the atmosphere only through a relatively thin surface layer.

The physical justification for this model, especially the basis for dividing the biota into two reservoirs, is discussed in greater detail by Keeling.[5] The use of spatially averaged properties does not necessarily imply homogeneity or mixing within the reservoirs. Insofar as possible, the symbols correspond to those used by Bolin and Eriksson.[3]

INDUSTRIAL CARBON DIOXIDE

Combustion of fossil fuels presently accounts for most of man's industrial and domestic energy production. The rate of combustion has been rising since the 18th century at about 4% per year except during the great economic depression and two world wars of the present century. Even if nuclear fuels or solar energy gradually displace fossil fuel as man's dominant source of energy, demand for fossil fuel is likely to continue to rise as industrialization spreads to

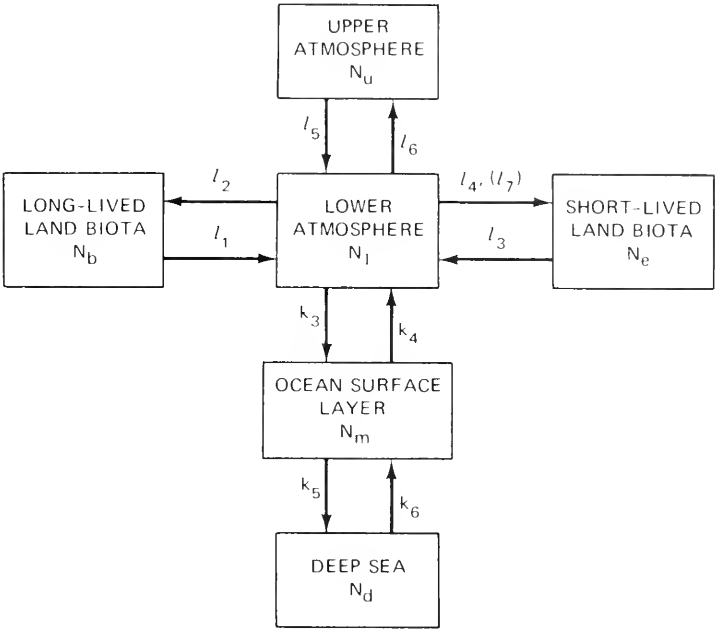

Fig. 1 Diagrammatic representation of the six-reservoir model of CO_2 exchange. Arrows represent the direction of fluxes between reservoirs. The N_i denote carbon masses for each reservoir. In the five-reservoir model (not shown), the upper and lower atmosphere are combined to form a single atmospheric reservoir. Transfer coefficients k_i and l_i are defined in Appendix C.

more and more nations. Continued exponential growth probably will not be limited by vanishing resources until well into the 21st century and possibly for as long as another hundred years. Exponential growth typically continues until nearly half of a natural resource is exhausted.[12] The ultimate production of coal, petroleum, and natural gas, as estimated by Hubbert,[12] would release five to nine times as much carbon as the preindustrial atmosphere contained. If Hubbert's lower limit is correct, 4% per year growth is possible until about 2040. Left out of Hubbert's estimates are the very large deposits of oil shales, which contain several hundred times as much carbon as the preindustrial atmosphere. If even a small portion of these is exploited, exponential growth may continue considerably longer than indicated by Hubbert's upper limit, even as far into the future as 2070, by which time a 4% per year growth would have released into the atmosphere CO_2 equivalent to eight times the preindustrial atmosphere level.

Industrial CO_2 production data used in this study are from an analysis by Keeling[13] of data assembled by the United Nations for the period 1860 to 1969 (Fig. 2). For essentially all industrial CO_2 produced before 1860 to be included, an exponential relation, derived from the data up to 1900, was extrapolated

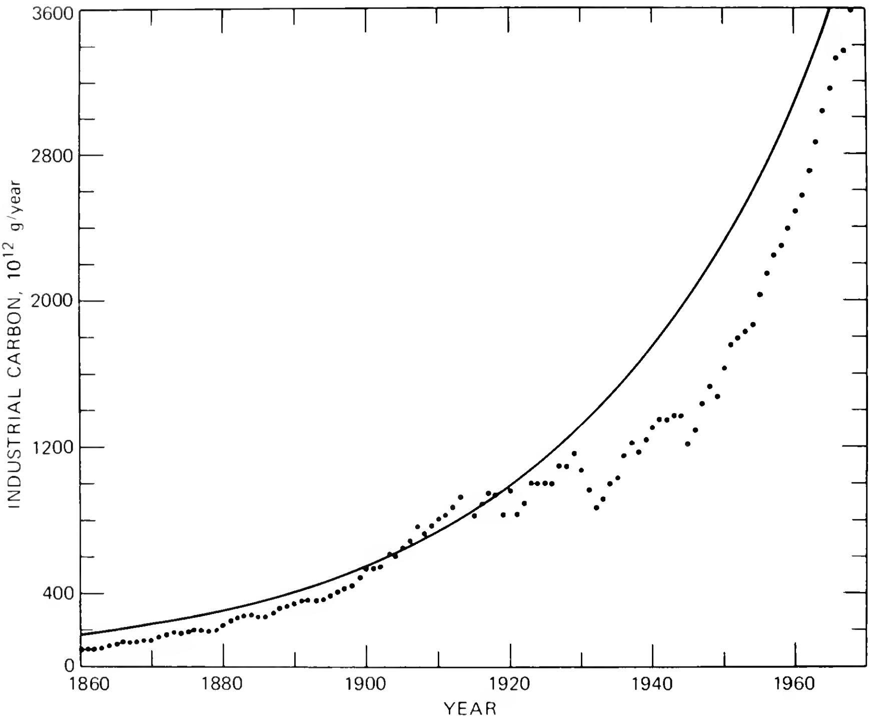

Fig. 2 Industrial carbon dioxide production since 1860. The solid curve is an exponential function with a growth of about 3% per year used by Bolin and Eriksson[3] in their model.

backward from 1860 to 1700. For projections beyond 1970, a 4% growth rate in yearly industrial CO_2 was assumed. The recalculated annual values of Keeling for CO_2 production are about 13% lower than those of Revelle[14] and of the Study of Critical Environmental Problems[15] because delayed or incomplete combustion is taken into account and because the carbon content of lignite was overestimated in the earlier studies. Keeling[13] estimates that systematic errors contribute about ±15% uncertainty to the recalculated production data.

ATMOSPHERIC CARBON DIOXIDE

Accurate direct observations of atmospheric CO_2 are available for approximately the past 15 years. The longest and most continuous records,[7] obtained at Hawaii and the South Pole, indicate for 1959 to 1969 an atmospheric CO_2 increase of 2.34% ± 0.20 relative to preindustrial times, and an airborne fraction of industrial CO_2 of 49% ± 12. Over half the uncertainty in the airborne fraction is related to the estimation of industrial CO_2 production.

RADIOCARBON OBSERVATIONS AND THE SUESS EFFECT

Radiocarbon, ^{14}C, is formed in the upper atmosphere by cosmic-ray collisions. It then mixes with inactive carbon in the atmosphere, the oceans, and the land biota. Its mean life[16] of 8267 years makes it a convenient tracer for studying the short-term natural carbon cycle. Fossil fuel, owing to long underground storage, contains practically no ^{14}C. Nevertheless, its combustion dilutes and displaces the ^{14}C in all the earth's reservoirs where ^{14}C occurs naturally. The relative depletion for the atmospheric reservoir, often called the Suess effect, has been determined from the radiocarbon/inactive carbon ratio ($^{14}C/C$) in independently dated wood. This effect has been measured by Suess and his coworkers,[17,18] Fergusson,[19] and Lerman, Mook, and Vogel,[20] among others. After 1954, nuclear bomb tests complicated matters by also introducing ^{14}C into the atmosphere. We have considered ^{14}C data only up to 1954.

During this year the Suess effect was approximately −2.3% ± 0.4 if we follow the practice of counting only the variation in ^{14}C since a late 19th century base-line period. A relatively high uncertainty is implied by the different average values obtainable from the data of individual investigators. If we extrapolate to 1954 tree-ring data for the period 1945 to 1954, we find that seven analyses reported by Houtermans et al.[18] of one tree at 45°N yield a value of about −2.7%, single analyses of seven trees in both hemispheres by Lerman et al.[20] yield about −2.3%, and six analyses of four trees in both hemispheres by Fergusson[19] (extrapolated by that author) give −2.0%. As we discuss later, about −0.3% is to be added to the above figures if we are to include the industrial dilution from the beginning of industrialization to the late 19th century. This leads to a corrected Suess effect in 1954 of −2.6% ± 0.4. These extrapolations do not take into account a probably negligible decrease in radiocarbon between the late 1940s and 1954 which may have occurred as a result of heliomagnetic perturbations of the cosmic-ray flux, as discussed later.

The average $^{14}C/C$ ratios of surface and deep-ocean water for 1954 can be estimated from fractionation-corrected data compiled by Broecker.[21] These data, as published, were normalized for departures of the $^{13}C/^{12}C$ ratio of each sample from a standard value of that ratio. It is not possible from the normalized data to deduce exactly the radioisotopic ratios of the original samples, but the correction for fractionation can be approximately cancelled using independent observations of $^{13}C/^{12}C$ in seawater, such as reported by Craig.[22] We deduce that the actual $^{14}C/C$ ratios relative to the ^{14}C standard (as discussed in a later section) were 0.999 ± 0.019 and 0.86 ± 0.04 in 1954 for surface and deep-ocean water, respectively. If the $^{14}C/C$ ratio of the standard were normalized to the $^{13}C/^{12}C$ ratio of atmospheric CO_2, these ratios would be 0.963 ± 0.020 and 0.83 ± 0.04, respectively. The quoted uncertainties are as stated by Broecker et al.[8]

MODEL EQUATIONS

The equations for the model (Appendixes A, B, and C) express material balances for each reservoir. The fluxes between reservoirs are, with the exceptions noted in this paragraph, taken to be proportional to the total carbon in the reservoir from which they originate. The exchange of carbon between the ocean surface layer and the deep ocean takes place by both water exchange and a constant downward gravitational transport of particulate carbonaceous matter. The return flux to the atmosphere from the ocean surface layer is proportional to the partial pressure of CO_2 exerted by the surface layer in accordance with the law of gas exchange.[23] The exchange of carbon between the atmosphere and the land biota also forms an exception, as discussed in a later section.

Each flux of ^{14}C is obtained by multiplying the corresponding flux of inactive carbon by the isotopic mass or pressure fraction of ^{14}C in the originating reservoir and by an isotopic fractionation factor that differs from unity by no more than a few percent. The transfer coefficients are always treated as input parameters. The preindustrial $^{14}C/C$ ratios are consequently derived by the model (see Eqs. B.4 to B.9 of Appendix B).

Industrial CO_2 production, entered into the rate equations as a carbon source for the lower atmosphere beginning with the year 1700, drives the entire model. The sources that cause variations in the ^{14}C system are the inactive-carbon perturbations, particularly the increase in total carbon in the ocean surface layer. (In Appendixes B and C, these are called virtual sources.) For all calculations not otherwise described, we assume, in addition to the steady-state production of ^{14}C, a variable ^{14}C source in the upper atmosphere to represent a heliomagnetic effect correlated with sunspot numbers, beginning with the year 1500 (Appendix C). This latter source is expressed as a perturbation and is required to sum to zero over the period 1500 to 1960 for which sunspot data are available. It introduces small fluctuations with periods of approximately 11 and 85 years, as discussed in the preceding paper (Ekdahl and Keeling[7]).

In the following sections we explain the basis for the nonlinear equations of the model. A detailed explanation of the linear equations appearing in the appendixes is given by Keeling.[5]

EVASION FACTOR

The mass-balance equations which connect the atmosphere and surface ocean water involve a relationship between the partial pressure of CO_2 exerted by the ocean surface water, P_m, and the total inorganic carbon in this water, ΣC. A mathematically convenient form of this relation is represented by the evasion factor, ξ,

$$\xi = \left[\frac{(P_m - P_{m0})/P_{m0}}{(\Sigma C - \Sigma C_0)/\Sigma C_0}\right]_{\text{constant alkalinity}} \tag{1}$$

where P_{m0} and ΣC_0 are preindustrial values of P_m and ΣC. The evasion factor depends on the dissociation quotients of carbonic acid, boric acid, and water in seawater, the hydrogen-ion concentration, the total boron concentration, ΣC, and the alkalinity. For an average surface water (Appendix D), all these factors remain unchanged when CO_2 is added to seawater except hydrogen-ion concentration and ΣC. The alkalinity is constant because total ionic charge is unaffected by adding or removing the uncharged species CO_2. For any given value of ΣC, the hydrogen-ion concentration in average surface water is found using the equations in Appendix D, and then ξ is evaluated. At the beginning of the industrial era, the evasion factor was identical to the factor $d(\ln P_m)/d(\ln \Sigma C)$ of Bolin and Eriksson.[3] If industrial CO_2 production continues to increase, however, ξ will rise with P_m according to the relation shown in Fig. 3. At the same time the short-term capability of the oceans to absorb CO_2 from the atmosphere will diminish.

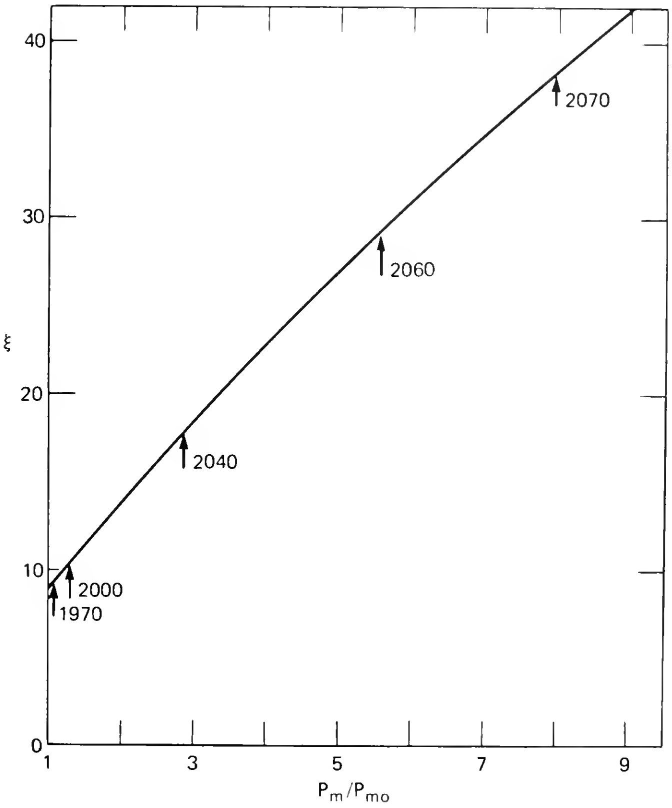

Fig. 3 Variation in evasion factor (ξ) for average ocean surface water as a function of CO_2 partial pressure relative to preindustrial times. (The date arrows are for the preferred model discussed later in text for which $\beta = 0.44$, $\tau_{am} = 7$ years, $\tau_{dm} = 1500$ years, and $N_{m0}/N_{a0} = 4$.)

LAND-BIOTA GROWTH FACTOR

It is not clear to us how best to model an increasing land biota, either to explain past perturbations in the carbon cycle or to make future predictions. Lacking detailed information on plant responses to changes in atmospheric CO_2 concentration, we have assumed the flux from the atmosphere to the long-lived biota, F_{ab}, and the return flux, F_{ba}, to be proportional to the total carbon in the long-lived biota, N_b. The model thus conforms to an intuitive picture that the long-lived biota grows and respires in proportion to the mass of long-lived plants. Roughly in accordance with the response of annual plants in glass-houses,[24-29] we further assume that the flux from the atmosphere increases as the logarithm of the atmospheric carbon mass, N_a. Thus we write

$$F_{ab} = F_{bo}\left[1 + \beta \ln\left(\frac{N_a}{N_{ao}}\right)\right]\left(\frac{N_b}{N_{bo}}\right) \tag{2}$$

$$F_{ba} = F_{bo}\left(\frac{N_b}{N_{bo}}\right) \tag{3}$$

where F_{bo} is the preindustrial (steady state) value of F_{ab} and F_{ba}, and N_{ao} and N_{bo} are preindustrial values of N_a and N_b. The factor β is an adjustable parameter that reflects the degree of CO_2 fertilization; it will be called the biota growth factor. For small increases in N_a and N_b, as have occurred up to now, if Eqs. 2 and 3 hold, the net flux to the long-lived biota is given to a close approximation by

$$F_{ab} - F_{ba} = \beta F_{bo}\left(\frac{N_a - N_{ao}}{N_{ao}}\right) \tag{4}$$

i.e., if the atmospheric CO_2 concentration increases by x %, the long-lived biota assimilates carbon at a net rate βx% higher than in the preindustrial atmosphere.

The formulations of the fluxes to and from the short-lived biota, F_{ae} and F_{ea}, are similar, except that F_{ae} is taken as proportional to the carbon mass of the long-lived biota, N_b, because well over half the short-lived biota growth is associated with long-lived plants:

$$F_{ae} = F_{eo}\left[1 + \beta \ln\left(\frac{N_a}{N_{ao}}\right)\right]\left(\frac{N_b}{N_{bo}}\right) \tag{5}$$

$$F_{ea} = F_{eo}\left(\frac{N_e}{N_{eo}}\right) \tag{6}$$

where F_{eo} is the preindustrial value of F_{ae} and F_{ea}, and N_{eo} is the preindustrial value of N_e. Because Eq. 5 implies a considerably greater restraint on the growth of short-lived plants than a similar expression with F_{ae} proportional to the carbon mass of the short-lived biota, N_e, the growth factor, β, is considerably larger for a given uptake of industrial CO_2 than if both biota reservoirs grew in proportion to their own masses, as assumed in the preceding paper (Ekdahl and Keeling[7]). The effect of this difference in assumption can be seen by comparing their Fig. 22 with our Fig. 6.

ISOTOPIC STANDARD FOR RADIOCARBON

We wish to compare ^{14}C variations of atmospheric CO_2 calculated by our model with ^{14}C variations of wood given in the literature. The latter are conventionally expressed relative to an age-corrected oxalic acid standard normalized to the $^{13}C/^{12}C$ ratio of average wood.

$$Su_w \equiv \frac{R_w}{R_\bullet} - 1 \tag{7}$$

whereas variations evaluated by the model are computed relative to preindustrial times

$$Su_l \equiv \frac{R_l}{R_{l\circ}} - 1 \tag{8}$$

In Eqs. 7 and 8, R denotes a $^{14}C/C$ ratio, observed or predicted, and the subscript l refers to the lower atmosphere, w to a wood sample, $\bullet$ to the standard, and $\circ$ to preindustrial times. To eliminate variations in ^{14}C content of wood owing to variations in isotopic fractionation during photosynthesis, and possibly during the preparation of samples, the values of R_w are normalized to the same $^{13}C/^{12}C$ ratio as that of the oxalic acid standard.

The two variations Su_w and Su_l, to a very good approximation, are related by an additive constant, $\delta_{\bullet\circ}$. Data listed for the base-line period in Table 1 are used to evaluate $\delta_{\bullet\circ}$ for a particular model.

Let Su_{w82}, defined equal to $(R_{w82}/R_\bullet) - 1$, denote the average of the ^{14}C variations of wood relative to the oxalic acid standard for the years of the base-line period of Table 1 (the weighted average date is 1882). Also, let Su_{l82}, defined equal to $(R_{l82}/R_{l\circ}) - 1$, denote the average of the ^{14}C variations of atmospheric CO_2 calculated by the model relative to preindustrial times for the years of the base-line period of Table 1. To establish a value for $R_{l\circ}$, we assume that the model predictions are in exact agreement with the observations for the base-line period

$$R_{l82} = \alpha_{wa} R_{w82} \tag{9}$$

where α_{wa}, with a value[5] of about 1.039, is the ^{14}C fractionation factor between average wood and atmospheric CO_2. Then

$$\frac{R_{l\circ}}{R_\bullet} = \frac{\alpha_{wa} R_{w82}/R_\bullet}{R_{l82}/R_{l\circ}} = \frac{\alpha_{wa}(1 + Su_{w82})}{1 + Su_{l82}} \equiv \alpha_{wa}(1 + \delta_{\bullet\circ}) \tag{10}$$

Since $Su_{\bullet 82}$ and Su_{l82} are both of the order of 1%,

$$\delta_{\bullet\circ} \simeq Su_{w82} - Su_{l82} \tag{11}$$

To calculate by model the ^{14}C/C variations of wood relative to standard for any specific period, e.g., the industrial period of Table 1, we assume consistent with Eq. 9

$$\mathrm{Su_w} = \frac{R_w}{R_\bullet} - 1 = \frac{R_l}{R_{l\circ}} \frac{R_{l\circ}}{\alpha_{wa} R_\bullet} - 1 = (1 + \mathrm{Su_l})(1 + \delta_{\bullet\circ}) - 1 \simeq \mathrm{Su_l} + \delta_{\bullet\circ} \tag{12}$$

The value of $\delta_{\bullet\circ}$ varies from model to model, but, for realistic values of the parameters, the value is between 0.2 and 0.3%.

The predicted ^{14}C/C ratios of oceanic carbon are similarly expressed relative to the oxalic acid standard for comparison with published data, after cancellation of the ^{13}C/^{12}C normalization of these data as discussed earlier.

$$\frac{R_m}{R_\bullet} = \frac{R_m}{R_{l\circ}} \frac{R_{l\circ}}{R_\bullet} = \frac{R_m}{R_{l\circ}} \alpha_{wa}(1 + \delta_{\bullet\circ}) \tag{13}$$

$$\frac{R_d}{R_\bullet} = \frac{R_d}{R_{l\circ}} \frac{R_{l\circ}}{R_\bullet} = \frac{R_d}{R_{l\circ}} \alpha_{wa}(1 + \delta_{\bullet\circ}) \tag{14}$$

TABLE 1

RADIOCARBON CONTENT OF DATED WOOD RELATIVE TO STANDARD*

Average date of samples	Total number of tree rings	Number of samples	$\mathrm{Su_W}$ (Δ^{14}C), ‰	Ref.
		Base-Line Period		
1861	2	1	−3.0	20
1862	9	1	−0.4	20
1862	9	1	2.3	20
1894	1	1	0.6	20
1898	1	1	−2.3	20
1899	9	1	−0.2	20
1900	8	1	−1.6	20
		Industrial Period		
1945	4	4	−21.8	18
1947	9	1	−14.7	20
1948	8	1	−20.7	20
1948	3	3	−23.0	18
1949	7	1	−19.5	20
1950	7	2	−18.8	20
1951	4	2	−23.1	20

*Values of $\mathrm{Su_W}$, as defined in the text, are expressed on the conventional Δ^{14}C scale (see references) as the per mil deviations of the ^{14}C activity of the wood samples from an age-corrected oxalic acid standard. Both samples and standard have been normalized to the same ^{13}C/^{12}C ratio.

NUMERICAL CALCULATIONS

The inactive and radiocarbon equations given in Appendix C were stepped using a fourth-order Runge–Kutta procedure[30] with two steps per year until 1969, then four steps per year. The starting year was 1700 for the inactive carbon equations. In those models which included a heliomagnetic effect, as discussed below, the radiocarbon equations were started with the year 1500 so that ^{14}C levels in the model reservoirs in 1700 would be in approximate secular adjustment with the long-term influences of this effect. The interval from 1500 to 1700 was deemed to be adequate because the longest adjustment time in the model (excepting the 8267-year radioactive decay time) was found to be approximately 200 years by solving a linear algebraic five-reservoir model as described by Keeling.[5] The Runge–Kutta method was checked against this algebraic model.

The polynomial equation for hydrogen-ion concentration, which arises when evaluating ξ, was solved by Newton's method (see Appendix D).

EFFECT OF CHANGES FROM THE MODEL OF BOLIN AND ERIKSSON

It is useful to add details to a model in small steps so that one can learn what is important. Figure 4 shows such a progression, beginning with the results of Bolin and Eriksson[3] for a three-reservoir model (atmosphere, ocean surface layer, and deep ocean) and ending with our five-reservoir model (former reservoirs plus short- and long-lived biota) with a constant ^{14}C source. If the average $^{14}C/C$ ratios of surface and deep-ocean water are as quoted earlier, the air-to-sea transfer time, τ_{am} (the reciprocal of the transfer coefficient k_{am} defined in Appendix A), is about 5 years, and the deep-ocean to surface-layer transfer time, τ_{dm} (reciprocal of k_{dm}), is about 1500 years. The CO_2 records at Mauna Loa and the South Pole for 1959 to 1969, when compared with the total record of industrial CO_2 production, indicate that about 45% of the accumulated industrial CO_2 should have remained in the atmosphere in 1954. This is equivalent to an increase of 5% in atmospheric CO_2 abundance. As has been discussed, the Suess effect in 1954 relative to the preindustrial era was approximately −2.6%. We see that the curves labelled 1 in Fig. 4, the Bolin–Eriksson result, are quite far from agreeing with either the CO_2 increase or the Suess effect.

Bolin and Eriksson, in their mathematical solution, neglected a term that dies out after only a few years. Their solution should be a good approximation. However, they neglected the term before matching the solution to the initial conditions, and their result is not the same as it would have been had they first fit the initial conditions and then neglected the term. The exact solution (both curves 2) differs little in CO_2 increase in the atmosphere but predicts a significantly smaller Suess effect. Using the annual CO_2 production data (see

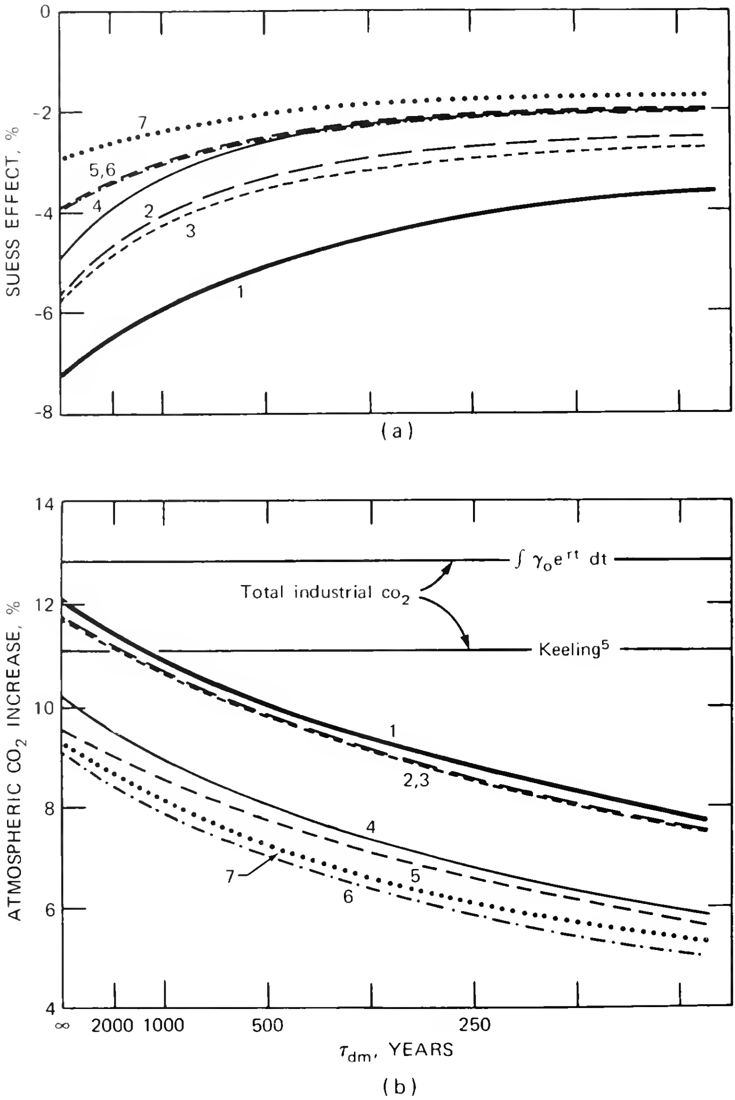

Fig. 2) instead of the considerably larger exponentially rising production values of Bolin and Eriksson (nearly 50% higher near 1954) further reduces the predicted Suess effect; including borate in the calculations and stepping ξ reduces it still further. After all these changes are made, the predicted Suess effect is close to the observed value, but the predicted CO_2 increase agrees with the expected value of about 5% only if the deep-ocean to surface-layer transfer time, τ_{dm}, is about 100 years, a time that is much too short.

Fig. 4 (a) The Suess effect in 1954 relative to preindustrial times as predicted by various reservoir models, all with τ_{am} = 5 years. (b) Predicted increase in inactive atmospheric CO_2 from 1700 to 1954 for the same models. Seven cases are shown, as follows:

Curve	Equation solving	Isotopic fractionation factors	CO_2 production	N_{mo}/N_{ao} *	Evasion factor	Land biota and ocean gravity flux
1	Approx.	=1	$\gamma_0 e^{rt}$ †	1.2	12.5	Neither
2	Exact	=1	$\gamma_0 e^{rt}$ †	1.2	12.5	Neither
3	Exact	Exact	$\gamma_0 e^{rt}$ †	1.2	12.5	Neither
4	Exact	Exact	Annual values	1.2	12.5	Neither
5	Exact	Exact	Annual values	2.0	12.5	Neither
6	Exact	Exact	Annual values	2.0	Stepped‡	Neither
7	Exact	Exact	Annual values	2.0	Stepped‡	Both

*Ratio of the preindustrial mass of inactive carbon in the surface ocean layer to that in the atmosphere.

†Exponential function of Bolin and Eriksson[3] with γ_0 = 0.000496 N_{ao}, r = 0.029 $year^{-1}$.

‡Varies from 8.9 to 9.2.

EMPIRICAL ADJUSTMENT OF THE MODEL

We now consider in some detail the consequences of attempting to adjust parameters until the model predictions agree as closely as possible with the principal observations: the observed CO_2 increase in the atmosphere, the decrease in atmospheric $^{14}C/C$ ratio deduced from recent measurements of dated wood, and the observed $^{14}C/C$ ratios of surface and deep-ocean water. Because the experimental data are uncertain, we must consider several possible combinations of parameters.

As a preliminary step, we vary over a wide range two parameters that significantly affect both the predicted inactive CO_2 increase and the Suess effect. These parameters are the deep-ocean to surface-layer transfer time, τ_{dm}, and the ocean surface-layer volume. The latter is expressed in terms of the ocean surface layer to atmosphere carbon ratio, N_{mo}/N_{ao}. As a second step we mutually adjust the atmosphere to ocean transfer time, τ_{am}, the ratio N_{mo}/N_{ao} again, and the biota growth factor, β, in a search for reasonable predictions of the Suess effect and atmospheric CO_2 increase. The model is now also forced to predict correctly the observed ^{14}C ratio of ocean surface water. As a final step we vary several parameters, one by one or in groups, to test the sensitivity of the model predictions to uncertainty in the observational data. Toward the end of this analysis, we abandon the observed Suess effect as a control on the choice of parameters and use instead estimates of the effective size of the ocean surface layer to limit the predicted Suess effect. Our final search for a good predictive model thus consists of choosing mutually acceptable values of the two parameters N_{m0}/N_{a0} and β, which most directly involve the ability of the oceans and biota to take up industrial CO_2. In these calculations we employ a six-reservoir model with two atmospheric reservoirs (Fig. 1) and with a heliomagnetic variation in ^{14}C source as discussed in a later section. To model the biota, we use the perturbation coefficients defined in Eq. C.35 of Appendix C.

To establish the best value for the Suess effect, we use recent data listed in Table 1 for the industrial period. The average relative to standard, weighted by the number of samples, we denote by the symbol Su_{48} because the average date is 1948. The value of Su_{48} is -2.11%. (If the older data of Fergusson[19] had been included, the value would have been somewhat less negative.) The corresponding Suess effect for 1954, as deduced by solving a model that exactly predicts the observed Su_{48}, is -2.51% relative to standard or -2.81% relative to preindustrial conditions. If one uses the same model but includes the effect of a heliomagnetic variation as discussed below, the predicted value of Su_{48} is changed slightly to -2.14%, and the $^{14}C/C$ ratio in 1954, relative to preindustrial conditions, is changed to -2.90%.

To model industrial CO_2, it would seem reasonable to define the ocean surface layer to include all the water that turns over at least once each year, i.e., approximately the water above the lowest depth attained annually by the thermocline. In temperate zones the thermocline[31] extends to about 100 m. It is shallower in the tropics but is deeper in polar regions where it may extend to the ocean bottom. Since 60 m of ocean water contains about the same total amount of carbon as the atmosphere, we evidently should assign to the model an ocean surface layer to atmosphere carbon ratio, N_{m0}/N_{a0}, of about 2. If we do so, however, we fail to take into account a layer of water between the thermocline and the 1000-m depth which is known to circulate more rapidly than the deep ocean below. The two-layer model can approximately reflect the exchange capability of this intermediate layer if the model's deep-ocean to surface-layer transfer time, τ_{dm}, is decreased from 1500 years or N_{m0}/N_{a0} is increased from 2.

The two curves in Fig. 5 show that the predicted correspondence of the atmospheric CO_2 increase and the Suess effect (expressed as Su_{48}) for variable τ_{dm} and N_{m0}/N_{a0} are strikingly close together. Apparently, for the purpose of calculating short-term atmospheric CO_2 variations, it does not matter precisely how the waters below the ocean surface layer are modeled. If we match the predicted atmospheric CO_2 increase to the observed value, we find τ_{dm} equal to about 100 years or N_{m0}/N_{a0} equal to about 15. These values almost surely exaggerate the role of intermediate water. Also, the corresponding model value of Su_{48} is only -1.3% (Suess effect of -1.7% in 1954 relative to preindustrial

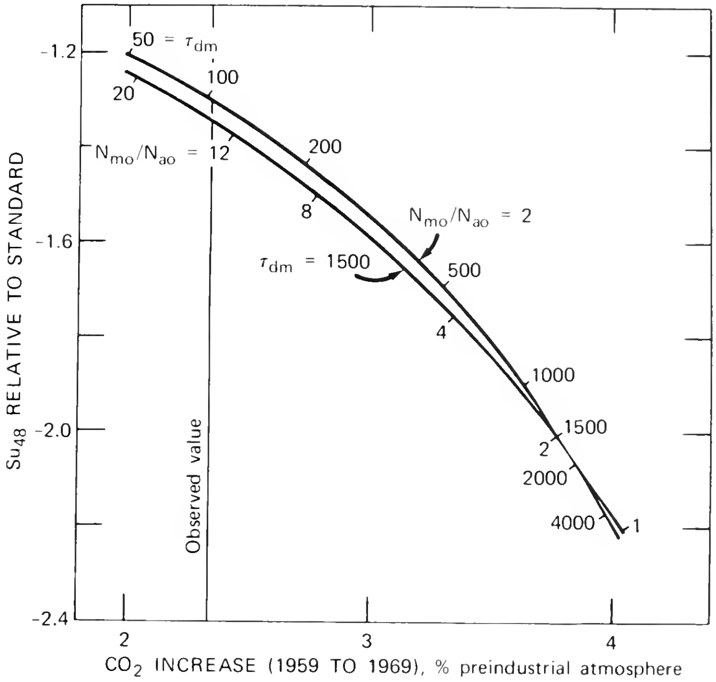

Fig. 5 Adjustment of the six-reservoir model to predict a given Suess effect relative to standard Su_{48}, or a given CO_2 increase in the atmosphere between 1959 and 1969. One curve was obtained by varying the deep-ocean to surface-layer transfer time, τ_{dm}; the other curve was obtained by varying N_{mo}/N_{ao}, the ratio of preindustrial carbon in the ocean surface layer to that in the atmosphere. If not varied, τ_{dm} was 1500 years and N_{mo}/N_{ao} was 2. The atmosphere–ocean transfer time, τ_{am}, was 6 years, and the biota was held to a constant size ($\beta = 0$).

conditions), compared with −2.1% (−2.8% in 1954) obtained from recent data. Indeed, to predict the observed Su_{48} exactly requires N_{m0}/N_{a0} less than 2 or τ_{dm} greater than 1500, in total disregard for the shorter circulation time of the intermediate water relative to deep water. Thus our attempt to reconcile the model predictions with both the observed Suess effect and the recent atmospheric CO_2 increase results in conflicting demands. The former suggests a surface layer that is too small; the latter suggests one that is too large.

The only means the model affords to reconcile the second discrepancy is to assume an increase in carbon stored in the land biota. We are aware that many biologists believe the land biota to be static or shrinking because of the destruction of forests and humus. The land biota is, nevertheless, a very complex system; a few percent increase could not be directly observed.

The most important consequences of postulating a positive biota growth factor can be deduced from Fig. 6 and Table 2. The curves, obtained by

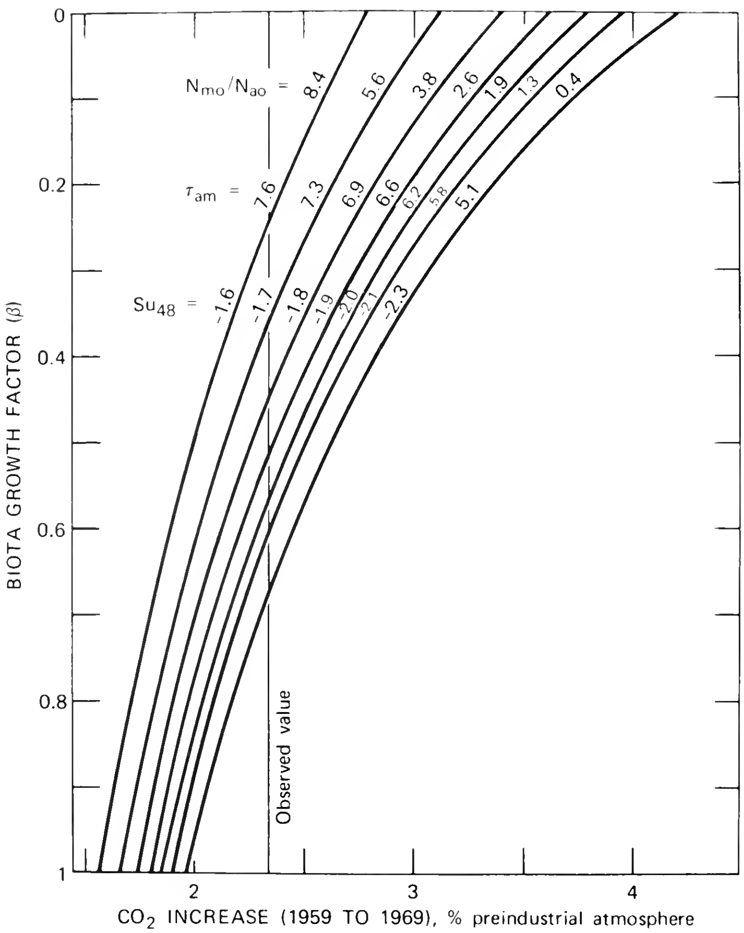

Fig. 6 Adjustment of the six-reservoir model with an increasing land biomass to fit preassigned values of the Suess effect relative to standard, Su_{48}, and $^{14}C/C$ ratio in ocean water, $R_m/R_\bullet$, relative to the oxalic acid standard for the year 1954. Su_{48} varies from -1.6 to -2.3%; $R_m/R_\bullet = 0.999$. Curves show the variation in the predicted CO_2 increase in the atmosphere between 1959 and 1969 as β varies for fixed values of τ_{am} and N_{mo}/N_{ao}. Su_{48} varies only negligibly for different values of β along a given curve. A small heliomagnetic effect (approximately -0.03%) has been included in the Su_{48} evaluations.

adjusting τ_{am}, N_{mo}/N_{ao}, and β to produce a prescribed value of Su_{48}, suggest that at present we cannot very precisely fix the size of the ocean surface layer from a knowledge of the Suess effect: to specify N_{mo}/N_{ao} within ±30% of its value would require that the Suess effect be known to ±0.05%. We may instead take the point of view that the model restricts the predicted value of the Suess effect if we require a reasonable value of N_{mo}/N_{ao}. On the basis of general

TABLE 2

SOLUTION OF THE SIX-RESERVOIR MODEL*

				Relative increase in carbon masses in 1954, %					^{14}C/C ratios		
Prescribed value of Su_{48}	Air–sea transfer time (τ_{am}), years	Growth factor (β)	Surface ocean to atmosphere carbon ratio (N_{m_0}/N_{a_0})	Land biota $\left(\frac{n_e + n_b}{N_{a_0}}\right)$	Atmosphere $\left(\frac{n_a}{N_{a_0}}\right)$	Surface ocean $\left(\frac{n_m}{N_{a_0}}\right)$	Deep ocean $\left(\frac{n_d}{N_{a_0}}\right)$	^{14}C/C difference in 1954 relative to preindustrial times† (Su), %	Surface ocean in 1700 $\left(\frac{R_m}{R_l}\right)$	Surface ocean in 1954 $\left(\frac{R_m}{R_l}\right)$	Deep ocean in 1700 $\left(\frac{R_d}{R_l}\right)$
−1.5	8.0	0.00	15.3	0.0	5.0	5.9	0.3	−2.09	0.965	0.961	0.814
−1.6	7.6	0.24	8.4	1.9	5.0	3.8	0.5	−2.20	0.968	0.962	0.816
−1.8	6.9	0.45	3.8	3.7	5.0	1.8	0.6	−2.45	0.972	0.961	0.820
−1.9	6.6	0.52	2.6	4.2	5.0	1.3	0.6	−2.59	0.975	0.961	0.822
−2.0	6.2	0.56	1.9	4.6	5.0	0.9	0.6	−2.73	0.977	0.961	0.824
−2.1	5.8	0.60	1.2	5.0	5.0	0.6	0.6	−2.86	0.979	0.960	0.826

*For all cases deep-ocean to surface-layer transfer time, τ_{dm}, is 1500 years, the ocean surface-layer ^{14}C/C ratio in 1954 relative to standard, $R_m/R_\bullet$, is 0.999, the 1959 to 1969 lower atmosphere CO_2 increase is 2.34% of N_{l_0}, and the evasion factor in 1954 is 9.1.

†Includes the heliomagnetic effect. If this effect were neglected, the Suess effect relative to preindustrial times would be less negative by approximately 0.09%.

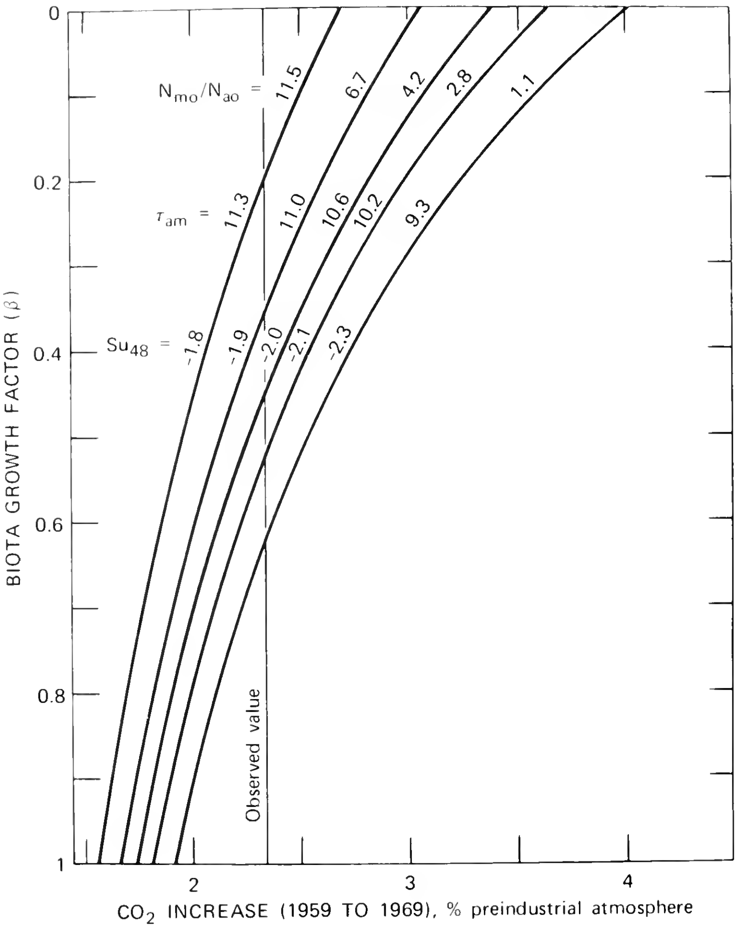

Fig. 7 Model-adjustment curves derived as in Fig. 6, except that $R_m/R_\bullet$ is fixed at 0.978.

considerations of the intermediate water circulation,[32] the effective value of N_{m0}/N_{a0} probably does not exceed 6. With a lower limit on N_{m0}/N_{a0} of 2, as discussed earlier, the true value of Su_{48} according to Fig. 6 lies between −1.7 and −2.0%.

This prediction, however, takes no account of uncertainties in other model parameters. The curves in Fig. 6 refer to models consistent with a relative $^{14}C/C$ ratio in the surface layer, $R_m/R_\bullet$, of 0.999 in 1954. If instead we adopt the lower limit of 0.978, we obtain the results shown in Fig. 7. For the same range of N_{m0}/N_{a0}, the Suess effect is more negative by about 0.2%. On the other hand, for a given value of N_{m0}/N_{a0}, the range in growth factor remains approximately the same (0.4 to 0.5 for values that predict approximately the observed atmospheric CO_2 increase from 1959 to 1969).

Our estimate of the overall mass of the land biota is also uncertain. Bowen's statement[33] that direct estimates of global biomass may be in error by ±50% is probably not an exaggeration. If we reduce by half the estimated 1.72×10^{18} g of carbon in the land biota and also reduce the fluxes F_{b0} and F_{e0} to preserve constant preindustrial transfer times, the predicted Suess effect becomes more negative by about 0.2% for given values of N_{m0}/N_{a0} and predicted atmospheric increase. At the same time the growth factor doubles. The mass flux ratios (transfer times) are at least as well determined as the masses so that the combined uncertainty in flux and mass is not much greater than the uncertainty already quoted on the basis of masses alone.

If we consider the ranges of uncertainty in N_{m0}/N_{a0}, $R_m/R_\bullet$, and biomass, the six-reservoir model predicts $Su_{48} = -1.8\% \pm 0.4\%$ and a Suess effect of $-2.5\% \pm 0.5\%$ in 1954 relative to preindustrial conditions. This latter prediction is slightly less negative than the 1954 extrapolation of the observed value of Su_{48} (−2.8%) and slightly more negative than the corresponding value based on the data of Fergusson (−2.3%) (Ref. 19). It is close to the extrapolated average of all these observations combined (−2.6%). The six-reservoir-model prediction is thus in as good agreement with the radiocarbon observations as could be expected considering the observational uncertainties.

Returning to the question of whether the land biota has increased in mass, no model with reasonable values of the model parameters predicts the observed atmospheric increase unless the growth factor, β, is positive. If we allow for the uncertainty in our estimate of the airborne fraction of the industrial CO_2 production and assume an upper limit of 6 for N_{m0}/N_{a0}, β could be as low as 0.05, as can be approximately deduced by assuming a ±25% error in the CO_2 increase as plotted in Figs. 6 and 7. Changing the assumed mass of the biota would change the value of β but not the amount of the predicted increase. Thus the observations, even though uncertain, support the hypothesis that the land biomass has increased at least for the period 1959 to 1969.

It is of course possible that the atmospheric CO_2 data for those years are not typical. The data, after the seasonal oscillations are removed, show a distinctly reduced slope in the years immediately following 1963 (best seen in Fig. 3 of the previous paper, Ekdahl and Keeling[7]). This reduced slope could have been a result of a surface ocean temperature decrease after 1963, and consequent anomalously low CO_2 pressures in surface water, and an abnormally high rate of CO_2 transfer to the oceans. Indeed, oceanic cooling has been observed[34] and could have been caused by the explosion of Mt. Agung in 1963. Volcanic debris was injected into the stratosphere where it persisted for several years and reduced solar radiation in both hemispheres.[35,36]

Another possibility is that our two-layer model of the ocean is too simple a representation. For example, no one, to our knowledge, has investigated whether an oceanic model with meridional circulation such as proposed by Eriksson[37] and Keeling and Bolin[38] might produce a relation between inactive and radioactive carbon in the atmosphere different from that shown in Fig. 5. Thus, without better measurements of the Suess effect and additional model formulations, we cannot demonstrate conclusively that the land biota has increased in mass during the recent past.

We find in conclusion that, although our calculations lead to some interesting speculations about past variations in ^{14}C and land biomass, we have been unable to determine precisely which reservoir, the oceanic or land plant, removes more industrial CO_2 from the atmosphere. The parameters most critical to this determination, N_{mo}/N_{ao} and β, cannot be fixed within narrow limits on the basis of the data we have used.

Machta (this volume)[39] further tests the six-reservoir model using more recent ^{14}C data. He does not attempt to fit closely the predicted and observed atmospheric CO_2 increase, but he obviously could do so by adjusting upward the biota growth factor, which he fixes at the value 0.25. He finds that the large observed variations in atmospheric ^{14}C produced by nuclear weapons tests after 1954 are best predicted by a model with N_{mo}/N_{ao} equal to about 2, in good agreement with our model when adjusted to predict the ^{14}C data before the nuclear era.

The nuclear era ^{14}C data used by Machta, although they furnish independent evidence of the rate of exchange of CO_2 between the atmosphere and the oceans and land biota, are not without their own shortcomings. The useful record is only a few years long, and the weapons produced ^{14}C unevenly dispersed, even within the atmosphere. The assignment of model parameters is sensitive to unavoidably rough estimates of annual changes in ^{14}C inventory. Imprecision in the nuclear-era data must produce uncertainty in Machta's estimate of N_{mo}/N_{ao}, but we do not know how much. We suspect that values of N_{mo}/N_{ao} as high as our tentative upper limit of 6 will produce acceptable predictions of nuclear-era ^{14}C variations. If so, the relative importance of the oceans and land biota to industrial CO_2 uptake is still an unsettled question.

PREFERRED MODELS

Since we cannot decide from present observational evidence how much increased growth to assign to the land biota, we will examine in detail two possible growth rates. We employ the six-reservoir model and the perturbation coefficients of Eq. C.36 of Appendix C. In the first model we adjust the atmosphere to surface-layer transfer time, τ_{am}, and the biota growth factor, β, to fit precisely: (1) a CO_2 increase in the atmosphere from 1959 to 1969 of 2.34% and (2) a $^{14}C/C$ ratio of ocean surface water in 1954 relative to standard, $R_m/R_\bullet$, of 0.999. The ocean surface layer to atmosphere carbon ratio, N_{mo}/N_{ao}, is set equal to 2 and the deep ocean to atmosphere transfer time,

τ_{dm}, is set equal to 1500 years (to agree approximately with the observed $^{14}C/C$ ratio of deep-ocean water). We find as best-fit values $\tau_{am} = 6.3$ and $\beta = 0.56$. The predicted Suess effect, Su_{48}, is -1.99%. In the second model we increase N_{m0}/N_{a0} to 4 and find as best-fit values $\tau_{am} = 7.0$ and $\beta = 0.44$. The predicted Su_{48} in this case is -1.80%. We could, of course, choose more cases, but these two are sufficient to illustrate the uncertainty in β and predicted Su_{48} as N_{m0}/N_{a0} is varied.

PREDICTIONS

If we assume the first preferred model and continued 4% annual increase in fossil-fuel combustion and if the land biota is now assumed to increase in mass according to the nonlinear equations Eqs. 2, 3, 5, and 6, the concentration of atmospheric CO_2 will reach 6.0 times its preindustrial level by 2070 (Fig. 8 and Table 3a). (The input is 8.00 N_{l0}, the atmospheric fraction 62.5%; consequently the atmospheric increase factor is $8.00 \times 0.625 + 1 = 6.0$.) If the ocean surface layer is assumed to be twice as large (second model, Table 3b), the predicted value is 6.3 ($=8.00 \times 0.664 + 1$). The first model implies that the biota almost doubles in mass in the next 100 years. The second model predicts a 70% increase in mass.

Actually a large increase in biomass is unlikely to occur in the next century. A rising demand for agricultural land and timber is almost sure to occur along

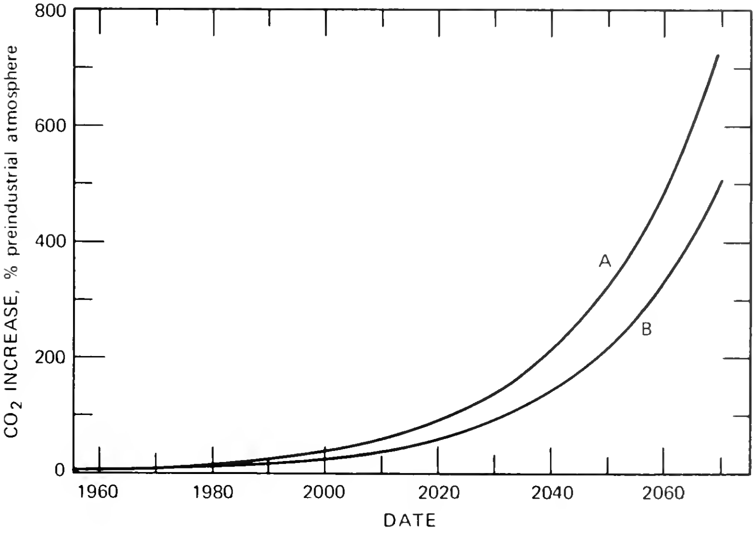

Fig. 8 Predicted CO_2 increase in the atmosphere for the model with $\tau_{am} = 6.27$ years, $N_{m0}/N_{a0} = 2$, $\beta = 0.556$, and $\tau_{dm} = 1500$ years. Curve A is with the biota growth stopped (β set to 0) in 1970; curve B is with no cutoff of biota growth.

TABLE 3a

PREDICTIONS OF FIRST MODEL*

Variable	With biota increase					No biota increase after 1970		
	1954	1970	2000	2040	2070	2000	2040	2070
Integrated Effects								
Total industrial CO_2 input as fraction of atmospheric CO_2 mass (N_{a0})	0.1114	0.1826	0.537	2.48	8.00	0.537	2.48	8.00
Total CO_2 partitioning, %								
Atmosphere	44.4	45.8	49.8	55.9	62.5	69.9	83.8	91.3
Biota	41.0	39.9	36.5	33.4	30.8	12.6	2.7	0.8
Oceans	14.6	14.3	13.7	10.7	6.7	17.5	13.5	7.9
Surface ocean evasion factor (ξ)	9.1	9.3	10.2	15.6	31.0	10.7	18.7	39.5
Inorganic carbon in surface water as fraction of initial value ($\Sigma C/\Sigma C_0$)	1.005	1.008	1.025	1.087	1.161	1.033	1.109	1.185
Hydrogen-ion concentration of surface water expressed as $-\log [H^+] \equiv pH$	8.256	8.245	8.19	7.96	7.60	8.17	7.87	7.47
Differential Effects								
Annual industrial CO_2 input as fraction of N_{a0}	0.0030	0.0063	0.0205	0.0983	0.3188	0.0205	0.0983	0.3188
Instantaneous CO_2 partitioning, %								
Atmosphere	42.8	50.1	53.1	60.9	68.0	82.2	91.2	96.3
Biota	42.9	35.9	34.2	31.4	28.6	0.0	0.0	0.0
Oceans	14.3	14.0	12.7	7.7	3.4	17.8	8.8	3.7
Surface ocean buffer factor (ζ)	9.4	9.7	11.7	26.2	82.8	12.9	36.8	113.1

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*τ_{am} = 6.27 years, τ_{dm} = 1500 years, N_{m0}/N_{a0} = 2.0, β = 0.556, $R_m(1954)/R_{\bullet}$ = 0.099, initial pH = 8.271.

TABLE 3b

PREDICTIONS OF SECOND MODEL*

	With biota increase					No biota increase after 1970		
Variable	**1954**	**1970**	**2000**	**2040**	**2070**	**2000**	**2040**	**2070**
			Integrated Effects					
Total industrial CO_2 input as fraction of atmospheric CO_2 mass (N_{a0})	0.1114	0.1826	0.537	2.48	8.00	0.537	2.48	8.00
Total CO_2 partitioning, %								
Atmosphere	45.2	46.3	49.8	57.1	66.4	63.9	77.3	87.4
Biota	32.2	31.4	28.6	25.7	23.0	10.0	2.2	0.7
Oceans	22.6	22.3	21.6	17.2	10.6	26.1	20.5	11.9
Surface ocean evasion factor (ξ)	9.1	9.3	10.1	15.5	32.0	10.5	17.8	38.3
Inorganic carbon in surface water as fraction of initial value ($\Sigma C/\Sigma C_0$)	1.005	1.008	1.024	1.087	1.164	1.030	1.104	1.182
Hydrogen-ion concentration of surface water expressed as $-\log[H^+] \equiv pH$	8.256	8.246	8.20	7.97	7.58	8.18	7.89	7.48
			Differential Effects					
Annual industrial CO_2 input as fraction of N_{a0}	0.0030	0.0063	0.0205	0.0983	0.3188	0.0205	0.0983	0.3188
Instantaneous CO_2 partitioning, %								
Atmosphere	44.0	49.8	53.1	63.7	74.4	73.5	86.3	94.6
Biota	34.3	28.4	26.6	23.8	20.4	0.0	0.0	0.0
Oceans	21.7	21.8	20.3	12.5	5.2	26.5	13.7	5.4
Surface ocean buffer factor (ζ)	9.4	9.7	11.5	26.2	86.8	12.3	33.7	109.0

*τ_{am} = 6.97 years, τ_{dm} = 1500 years, N_{mo}/N_{ao} = 4.0, β = 0.438, $R_m(1954)/R_\bullet$ = 0.999, initial pH = 8.271.

with the rising demand for fossil fuels. The prime causes for rising fuel demand are a rise in human living standards and increasing human population, and either of these will also raise the demand for food and timber during the next 100 years. The area of forests and perennial grass land will probably diminish at such a rate that the world biomass will be reduced at least as fast as CO_2 fertilization promotes an increase.[40]

Thus, the two preferred models almost surely overestimate the possible increase in biomass. The upper limit on biomass increase is probably so small that any increase is negligible compared to the input of industrial CO_2. If the biomass increase in the model is stopped in 1970, the predicted atmospheric CO_2 concentration in 2070 is about 30% higher than that quoted above; for the first model the predicted concentration is 8.3 and for the second model 8.0 times the preindustrial level. As shown by Table 4, these predictions are not greatly changed if the oceanic parameters are varied between limits suggested by the uncertainty in observational data. Varying the ocean parameters has still less influence on prediction if the biota is assumed to increase in mass after 1970.

As a final test of the relative roles of the oceans and land biota in long-range prediction, we considered the case where past variations in atmospheric CO_2 are explained solely by ocean uptake, i.e., the case $\beta = 0$, $N_{m0}/N_{a0} = 15.0$, $\tau_{am} = 7.9$ years, and $\tau_{dm} = 1500$ years. According to this extreme model, the atmospheric CO_2 concentration in 2070 will be 6.5 times the preindustrial level. Comparing this result with the previous two models, we see that the predicted atmospheric CO_2 concentration in 2070 is almost sure to fall between 6 and 8 times the preindustrial value, regardless of whether the biota increases or not.

Returning to the preferred models, the instantaneous and total partitioning of industrial CO_2 between major reservoirs, also shown in Tables 3a and 3b, furnishes a measure of the nonlinearity of the model. A linear model (see Eqs. 21 and 23 of the preceding paper, Ekdahl and Keeling[7]) would predict almost time invariant partitioning. As can be seen, the partitioning departs from near constancy only after the end of this century. Thus, to make short-term predictions of the atmospheric CO_2 increase, as Machta has done,[39] it is not essential to know how the industrial CO_2 is shared between the oceans and land biota: regardless of which reservoir is taking up most of the CO_2, the airborne fraction will probably not change significantly. This near constancy in fraction depends, of course, on the plausible assumptions that fossil-fuel combustion continues to increase at nearly the same rate and that the land biota continues to respond in the same manner for the next few years as during the recent past.

The instantaneous rate of change of CO_2 partial pressure with increasing total carbon in surface water relative to initial conditions

$$\zeta = \frac{dP_m/P_{m0}}{d\Sigma C/\Sigma C_0} \tag{15}$$

we refer to in the tables as the surface ocean buffer factor. It is more indicative of the ocean surface water affinity for industrial CO_2 than is the evasion factor,

TABLE 4

EFFECT OF VARIATIONS OF PARAMETERS ON PREDICTIONS OF SIX-RESERVOIR MODEL*

Transfer times							
Air–sea (τ_{am}), years	Deep ocean–surface ocean (τ_{dm}), years	Surface-layer-atmosphere carbon ratio (N_{mo}/N_{ao})	Atmospheric CO_2 abundance relative to preindustrial era (N_a/N_{ao})				
			1954	1970	2000	2040	2070
			No increase in biota after 1970				
5 to 10†	1500	2	1.050	1.084	1.37	3.08	8.30
5 to 10	1000	2	1.048	1.082	1.36	3.03	8.18
5 to 10	1500	4	1.046	1.078	1.34	2.92	7.99
5 to 10	1500	6	1.043	1.073	1.31	2.76	7.68
			Biota increase through 2070				
5 to 10	1500	2	1.050	1.084	1.26	2.39	6.00

*For all cases the biota growth factor, β, is 0.556.

†N_a/N_{ao} varies with τ_{am} only in the third decimal place, e.g., for this case in 2070, τ_{am} = 5 and 10 gives N_a/N_{ao} = 8.296 and 8.300, respectively.

ξ, defined in Eq. 1, because it expresses the immediate pressure response of the water to added CO_2, whereas ξ expresses the slowly varying average response since preindustrial times. Given continued 4% annual increase in fossil-fuel combustion, the model predicts that ζ will increase more than 10-fold in the next century. In consequence of this increase not more than 6% of the industrial CO_2 produced in 2070 will enter the oceans that same year whether the biomass remains static or grows in size.

HELIOMAGNETIC EFFECT ON RADIOCARBON PRODUCTION

In the preceding calculations of the six-reservoir model, we assumed a variable production of radiocarbon in the stratosphere, as provided by Lingenfelter's ^{14}C production equations,[41] and the annual sunspot record after 1500 (Fig. 9, Appendix F). The results of the calculations are compared in Fig. 10 with a similar calculation ignoring the possible sunspot effect. The predicted fluctuations are small (as anticipated in the preceding paper, Ekdahl and Keeling,[7] and would be hard to detect, given the scatter in the present data (see Fig. 11). The agreement is not nearly so good as Grey and Damon[42] found (Fig. 12 of the preceding paper, Ekdahl and Keeling[7]) after adjusting their single exchange time. Our results indicate a negligible correction (−0.03%) needs to be added to the Suess effect parameter Su_{48}. The correction for 1954 is only slightly greater (−0.09%). Of course, it is possible that the Lingenfelter equation underestimates the heliomagnetic effect upon ^{14}C production and that larger corrections should be applied.

The time-varying atmospheric $^{14}C/C$ ratio, its correlation with sunspots, and the Suess effect could be better understood if we had high-quality tree-ring data for the entire period after 1750. Houtermans et al.[18] and Lerman et al.[20] have demonstrated that high-quality data can be obtained by existing techniques. Such data would add to our confidence in modeling ^{14}C variations and hence to our understanding of the carbon cycle.

SUMMARY AND CONCLUSIONS

In a search for a reasonable prediction of changes in atmospheric CO_2 concentration over the next 100 years, we have explored the relationships between parameters of a six-reservoir geochemical model and observable quantities. The increase in atmospheric CO_2 concentration over approximately the past 10 years establishes the fraction of industrial CO_2 recently remaining airborne but offers no clue as to whether the remaining industrial CO_2 has entered the oceans or has been incorporated in land plants. We initially hoped to use measurements of radiocarbon to establish the fraction that enters the oceans, and we were encouraged to find that the model predicted the industrial dilution of atmospheric radiocarbon (the Suess effect) within the experimental accuracy

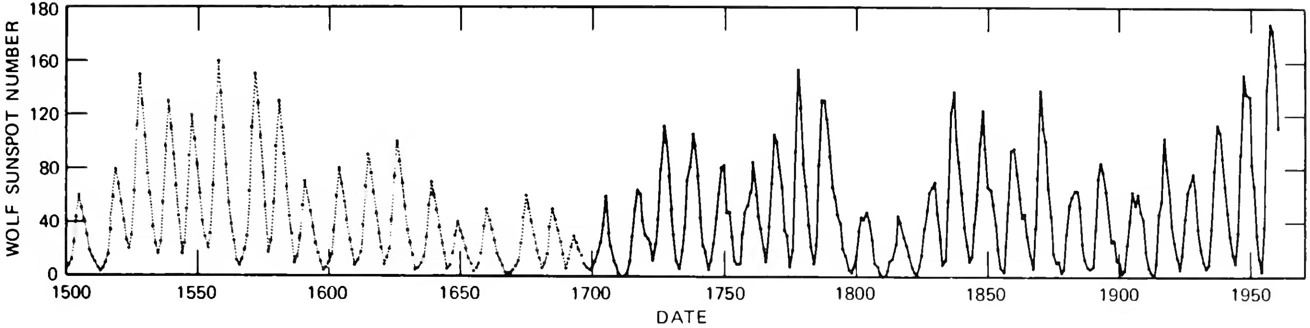

Fig. 9 Variation in annual number of sunspots from 1500 to 1960. The plot before 1700 is reconstructed from estimates given for years of maximum and minimum numbers.

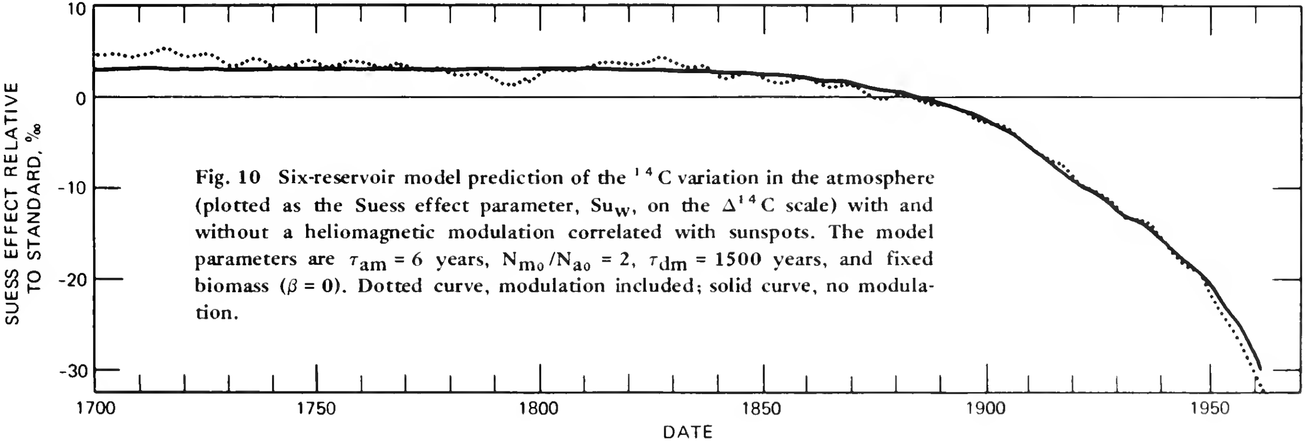

Fig. 10 Six-reservoir model prediction of the ^{14}C variation in the atmosphere (plotted as the Suess effect parameter, Su_W, on the Δ^{14}C scale) with and without a heliomagnetic modulation correlated with sunspots. The model parameters are $\tau_{am} = 6$ years, $N_{m_0}/N_{a_0} = 2$, $\tau_{dm} = 1500$ years, and fixed biomass ($\beta = 0$). Dotted curve, modulation included; solid curve, no modulation.

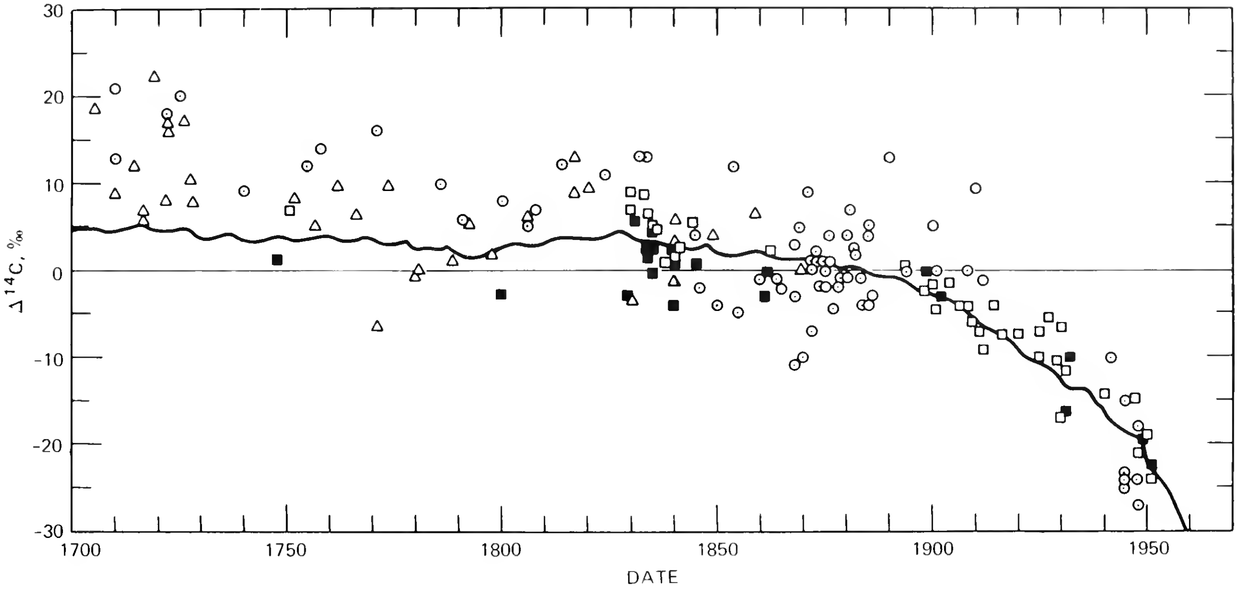

Fig. 11 Six-reservoir model prediction of the ^{14}C variation in the atmosphere (plotted as the Suess effect parameter, Su_W, on the $\Delta^{14}C$ scale) with a heliomagnetic modulation compared to ^{14}C data from dendrochronologically dated tree rings. Solid curve, modulation included (from Fig. 10). The sources of data are: □, Lerman et al.[20] (Northern Hemisphere); ■, Lerman et al.[20] (Southern Hemisphere); ⊙, Suess[17,43] (Northern Hemisphere); △, Stuiver[44] (Northern Hemisphere).

of the best available radiocarbon data. At the same time, we were disappointed to find that available radiocarbon data are not sufficiently accurate to establish the rate of oceanic uptake of CO_2 or, indeed, even to establish whether oceanic or biological uptake is the more important in reducing the airborne fraction of industrial CO_2.

To determine the CO_2 uptake by the oceans requires that not only the volume of the surface layer and the circulation time of deep water be known but also the rate of turnover of water lying at moderate depths below the surface layer. We were unable to establish this rate and hence the extent to which this intermediate water has taken up industrial CO_2. As an expedient we treated the volume of the surface layer as an adjustable parameter, ranging from approximately the correct value to a rough upper limit of three times that volume. Even with this upper limit, the model predicts that the land biota has taken up an appreciable fraction of the industrial CO_2 of recent years. This conclusion is weakened considerably, however, when we take into account the combined uncertainty of all the observational data, including the amount of industrial CO_2 actually produced and the radiocarbon content of surface ocean water.

It is ironical that mankind, by nuclear weapons testing, altered drastically the distribution of radiocarbon in the atmosphere, biota, and surface ocean water before scientists had had time to perfect methods to measure *natural* radiocarbon. If no artificial radiocarbon had been produced, the atmospheric Suess effect would today be so large that it could be measured to high precision, and additional ^{14}C measurements of land plants and surface water could provide data to establish within narrow limits the other critical parameters of a geochemical model.

We are instead severely limited as to what new data we can obtain. Our model analysis, although inconclusive, at least defines what additional data may still be sought with the best return for the effort. Owing to the complexity of the land biota, we cannot expect to obtain precise estimates of change in biomass directly. The best remaining approach is to make the optimum use of the historical record of atmospheric ^{14}C in tree rings. Our model suggests that a detailed time series from several carefully selected trees could improve the control on model parameters. One may argue that the relatively high counting errors for individual samples are a serious obstacle to detecting the small historical Suess effect. This is not a valid objection, however, because these errors are essentially random, and we need know only the global mean Suess effect averaged over several years. This time–space average can be based on so extensive a series of individual analyses that random errors contribute little to the uncertainty. A less apparent obstacle is to eliminate systematic errors arising from choosing trees that do not correctly reflect atmospheric variations. Matching of long-time series from each tree would be the best means to remove unrepresentative trees and at the same time would establish whether or not a measurable correlation with sunspots actually exists. We are aware that a major laboratory effort is required. Our model predictions, we hope, may provide motivation for intensifying the effort already begun.

As for the prediction of atmospheric CO_2 increase in the next century, the nonlinear CO_2 transfer equations for seawater indicate unambiguously that the world oceans will become progressively less able to absorb new increments of industrial CO_2, regardless of whether the oceans absorbed much or little industrial CO_2 in the past. Understanding ocean behavior is, however, only half the problem; for a valid prediction we also need to know whether the biomass of land plants will change in the next century. In our model we assume that the land biota responds to gaseous CO_2 approximately as do individual plants grown in glasshouses with adequate light, water, and nutrients. If this assumption holds, the land biomass (including detritus) may nearly double by 2070. More likely, however, the biota, as well as the oceans, will be less and less able to absorb new increments of industrial CO_2 because of competition between plants and changing land use by man. But, even if the conditions for land biomass increase are optimum, plant growth will not be able to keep pace with a rising rate of consumption of fossil fuels. If present industrial trends continue, the concentration of atmospheric CO_2 will rise to at least six times its preindustrial level during the next hundred years. If the biota does not respond appreciably to higher CO_2 concentrations in the air, the rise may be to over eight times the preindustrial level.

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APPENDIX A: GENERAL TIME-DEPENDENT EQUATIONS FOR THE SIX-RESERVOIR MODEL

Inactive Carbon Svstem

The governing equations for interacting inactive carbon pools have the general form

$$\frac{dN_i}{dt} = \sum_{j \neq i} (F_{ji} - F_{ij}) + \Gamma_i \qquad (A.1)$$

where the sum denoted by Σ is over all reservoirs j adjacent to reservoir i, N_i refers to the mass of carbon in reservoir i (i = u, b, e, l, m, or d in accordance with the notation of Fig. 1), t is the time, F_{ij} denotes the flux of carbon from reservoir i to j, and Γ_i denotes the CO_2 production rate in reservoir i. $\Gamma_i = 0$ except for the lower atmosphere, for which $\Gamma_l \equiv \gamma$.

Specifically:

Upper atmosphere

$$\frac{dN_u}{dt} = F_{lu} - F_{ul} = k_{lu}N_l - k_{ul}N_u \qquad (A.2)$$

Long-lived land biota

$$\frac{dN_b}{dt} = F_{lb} - F_{bl} \qquad (A.3)$$

Short-lived land biota

$$\frac{dN_e}{dt} = F_{le} - F_{el} \qquad (A.4)$$

Lower atmosphere

$$\frac{dN_l}{dt} = F_{ul} - F_{lu} + F_{el} - F_{le} + F_{bl} - F_{lb} + k'_{ma}P_m - k_{am}\frac{N_{a0}}{N_{l0}} N_l + \gamma \qquad (A.5)$$

Ocean surface layer

$$\frac{dN_m}{dt} = k_{am}\frac{N_{a0}}{N_{l0}} N_l - k'_{ma}P_m + k_{dm}N_d - k_{md}N_m - F_g \qquad (A.6)$$

Deep sea

$$\frac{dN_d}{dt} = k_{md}N_m + F_g - k_{dm}N_d \tag{A.7}$$

Water conservation

$$0 = k_{md}W_m - k_{dm}W_d \tag{A.8}$$

where k_{ul} = upper-atmosphere to lower-atmosphere transfer coefficient

k_{lu} = lower-atmosphere to upper-atmosphere transfer coefficient [the preindustrial equation leads to $k_{lu} = k_{ul}(N_{u0}/N_{l0})$]

k_{am} = air to sea transfer coefficient [defined in terms of the carbon mass of the total atmosphere; e.g., the preindustrial (steady-state) flux is $k_{am}N_{a0}$]

k'_{ma} = sea to air transfer coefficient (the preindustrial flux $k'_{ma}P_{m0}$ is numerically equal to $k_{am}N_{a0}$)

k_{md}, k_{dm} = surface-layer to deep-ocean and deep-ocean to surface-layer transfer coefficients, respectively

(All transfer coefficients, k_{ij}, are assumed to be time invariant.)

N_u, N_b, N_e, N_l, N_m, N_d = masses of inactive carbon in designated reservoirs

$N_a = N_u + N_l$ = mass of inactive carbon in the atmosphere as a whole

N_{u0}, N_{b0}, N_{e0}, N_{l0}, N_{m0}, N_{d0}, N_{a0} = masses of inactive carbon in the designated reservoir before the industrial era

$F_{lb} = F_{b0}[1 + \beta \ln(N_l/N_{l0})](N_b/N_{b0})$ = flux from lower atmosphere to long-lived land biota

F_{b0} = flux from lower atmosphere to long-lived land biota before industrial era and vice versa

β = land-biota growth factor (assumed to be time invariant)

$F_{bl} = F_{b0}(N_b/N_{b0})$ = flux from long-lived land biota to lower atmosphere

$F_{le} = F_{e0}[1 + \beta \ln(N_e/N_{e0})](N_b/N_{b0})$ = flux from lower atmosphere to short-lived land biota (taken as proportional to N_b/N_{b0} rather than N_e/N_{e0})

F_{e0} = flux from lower atmosphere to short-lived land biota before the industrial era and vice versa

$F_{el} = F_{e0}(N_e/N_{e0})$ = flux from short-lived land biota to lower atmosphere

P_m = CO_2 partial pressure in ocean surface layer

P_{m0} = value of P_m before the industrial era

γ = production rate of carbon in the atmosphere from industrial sources

$F_g = F_{g0}$ = gravitational flux of inactive carbon from ocean surface layer to deep sea (assumed to be time invariant)

W_m, W_d = volumes of ocean surface layer and deep ocean (assumed to be time invariant)

(All preindustrial quantities are assumed to be time invariant.)

Radiocarbon System

The governing equations A.2 to A.7 are replaced with six equations of the form

$$\frac{d{}^*N_i}{dt} + {}^*\lambda {}^*N_i = \sum_{j \neq i} ({}^*F_{ji} - {}^*F_{ij}) + {}^*\Gamma_i \tag{A.9}$$

where the sum is over all adjacent reservoirs, $^*\lambda$ is the radiocarbon decay constant, $^*N_i$ refers to the mass of radiocarbon in reservoir i, $^*F_{ij}$ refers to the flux of radiocarbon from reservoir i to j, and $^*\Gamma_i$ is the ^{14}C production rate in each reservoir. $^*\Gamma_i = 0$ except for the upper atmosphere, where a modulation, $^*\gamma$, correlated with sunspots is added to a steady-state term $^*\Gamma_0$ (see Appendixes B and C) to yield a total production rate

$$^*\Gamma_u = {}^*\Gamma_0 + {}^*\gamma \tag{A.10}$$

For certain specified calculations we assume $^*\gamma = 0$.

Specific fluxes are:

$$\left.\begin{aligned}
{}^*F_{ul} &= R_u k_{ul} N_u \\
{}^*F_{lu} &= R_l k_{ul} \frac{N_{u0}}{N_{l0}} N_l \\
{}^*F_{lb} &= \alpha_{ab} R_l F_{lb} \\
{}^*F_{bl} &= \alpha_{ba} R_b F_{bl} \\
{}^*F_{le} &= \alpha_{ab} R_l F_{le} \\
{}^*F_{el} &= \alpha_{ba} R_e F_{el}
\end{aligned}\right\}$$

(Eq. A.11
continued
on next page)

$$\left.\begin{aligned} {}^*F_{lm} &= \alpha_{am} R_l k_{am} \frac{N_{ao}}{N_{lo}} N_l \\ {}^*F_{ml} &= \alpha_{ma} R_{\tilde{m}} k'_{ma} P_m \\ {}^*F_{md} &= R_m k_{md} N_m + \alpha_{mg} R_{\tilde{m}} F_{go} \\ {}^*F_{dm} &= R_d k_{dm} N_d \end{aligned}\right\} \text{(Eq. A.11 continued)}$$

where $R_i = {}^*N_i/N_i$ = isotopic ratio of radioactive to inactive carbon in reservoir i

$R_{\tilde{m}}$ = isotopic ratio of radioactive *inorganic* carbon to inactive inorganic carbon in the surface ocean layer

R_m = similar ratio for combined inorganic and organic carbon in the surface ocean layer

α_{ab}, α_{ba} = isotopic fractionation factors associated with uptake and release of radiocarbon by the land biota (fractionation of long- and short-lived land biota are not differentiated)

α_{am}, α_{ma} = isotopic fractionation factors for ocean invasion and evasion of radiocarbon at ocean--atmosphere boundary

α_{mg} = isotopic fractionation factor for formation of particulate carbon in ocean surface layer

(All isotopic fractionation factors are assumed to be time invariant.)

In expressing the flux ${}^*F_{ml}$, we have neglected the very small variation in isotopic fractionation factor α_{am} with changes in the distribution of inorganic carbon species in surface water. This variation is discussed by Keeling.[5]

APPENDIX B: PREINDUSTRIAL ^{14}C EQUATIONS

Equations for preindustrial ^{14}C can be derived from Eq. A.9, the time-dependent equations, by setting the derivatives to zero and masses of carbon to their preindustrial values. The sum of these six equations, one for each reservoir, is

$${}^*\Gamma_0 = {}^*\lambda({}^*N_{uo} + {}^*N_{bo} + {}^*N_{eo} + {}^*N_{lo} + {}^*N_{mo} + {}^*N_{do}) \equiv {}^*\lambda \sum_i {}^*N_{io} \qquad \text{(B.1)}$$

where ${}^*\Gamma_0$ is the ^{14}C production rate in the upper atmosphere. This equation can be used to eliminate ${}^*\Gamma_0$ from the equation for the upper atmosphere

$$({}^*\lambda + k_{ul}){}^*N_{uo} - k_{ul} \frac{N_{uo}}{N_{lo}} {}^*N_{lo} = {}^*\Gamma_0 = {}^*\lambda \sum_i {}^*N_{io} \qquad \text{(B.2)}$$

It is convenient to eliminate the $^*N_{i0}$ via the identities

$$R_{i0} \equiv \frac{^*N_{i0}}{N_{i0}} \tag{B.3}$$

The preindustrial ^{14}C equations determine only ratios of the R_{i0}'s. For the six-reservoir model there are thus five independent equations:

$$R_{u0} = R_{l0} + \frac{^*\lambda}{k_{ul}N_{u0}} (R_{b0}N_{b0} + R_{e0}N_{e0} + R_{l0}N_{l0} + R_{m0}N_{m0} + R_{d0}N_{d0}) \tag{B.4}$$

$$R_{b0} = \frac{\alpha_{ab}}{\alpha_{ba}} \frac{R_{l0}}{1 + (^*\lambda N_{b0}/\alpha_{ba}F_{b0})} \tag{B.5}$$

$$R_{e0} = \frac{\alpha_{ab}}{\alpha_{ba}} \frac{R_{l0}}{1 + (^*\lambda N_{e0}/\alpha_{ba}F_{e0})} \tag{B.6}$$

$$R_{m0} = \alpha_{am} R_{l0} \left[\alpha_{ma} + \frac{^*\lambda}{k_{am}} \left(\frac{N_{m0}}{N_{a0}} + \frac{N_{d0}}{N_{a0}} \frac{\alpha_{dm}k_{dm}}{^*\lambda + k_{dm}}\right)\right]^{-1} \tag{B.7}$$

$$R_{d0} = R_{m0} \frac{\alpha_{dm}k_{dm}}{^*\lambda + k_{dm}} \tag{B.8}$$

where

$$\alpha_{dm} \equiv \alpha_{mg} + \frac{N_{m0}/W_m}{N_{d0}/W_d} (1 - \alpha_{mg}) \tag{B.9}$$

In Eqs. B.7 and B.8, we have made the approximation $R_{\tilde{m}0} = R_{m0}$. After each equation has been divided by R_{l0}, the relative ratios R_{i0}/R_{l0} can be evaluated in the following order: B.5, B.6, B.7, B.8, and then B.4.

APPENDIX C: PERTURBATION EQUATIONS

For numerical calculations, the equations of Appendix A are replaced by perturbation equations in terms of changes from the preindustrial state

$$n_i = N_i - N_{i0} \tag{C.1}$$

$$^*n_i = {^*N_i} - {^*N_{i0}} \tag{C.2}$$

We use Δ_{ij} and $^*\Delta_{ij}$ to denote the net flux of carbon and radiocarbon, respectively, from reservoir i to reservoir j, relative to the preindustrial state. We also introduce sets of coefficients k_i, l_i, $^*k_i$, and $^*l_i$ to simplify the writing of the perturbation equations.

Inactive Carbon System

Upper atmosphere

$$\frac{dn_u}{dt} = \Delta_{lu} \tag{C.3}$$

Long-lived land biota

$$\frac{dn_b}{dt} = \Delta_{lb} \tag{C.4}$$

Short-lived land biota

$$\frac{dn_e}{dt} = \Delta_{le} \tag{C.5}$$

Lower atmosphere

$$\frac{dn_l}{dt} = -\Delta_{lu} - \Delta_{lb} - \Delta_{le} + \Delta_{ml} + \gamma \tag{C.6}$$

Ocean surface layer

$$\frac{dn_m}{dt} = -\Delta_{ml} - \Delta_{md} \tag{C.7}$$

Deep sea

$$\frac{dn_d}{dt} = \Delta_{md} \tag{C.8}$$

where

$$\Delta_{lu} = -l_5 n_u + l_6 n_l \tag{C.9}$$

$$\Delta_{lb} = -l_1 n_b + l_2 n_l \tag{C.10}$$

$$\Delta_{le} = -l_3 n_e + l_7 n_b + l_4 n_l \tag{C.11}$$

$$\Delta_{ml} = -k_3 n_l + k_4 n_m \tag{C.12}$$

$$\Delta_{md} = -k_6 n_d + k_5 n_m \tag{C.13}$$

Radiocarbon System

Upper atmosphere

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_u = {}^*\Delta_{lu} + {}^*\gamma \tag{C.14}$$

Long-lived land biota

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_b = {}^*\Delta_{lb} \tag{C.15}$$

Short-lived land biota

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_e = {}^*\Delta_{le} \tag{C.16}$$

Lower atmosphere

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_l = -{}^*\Delta_{lu} - {}^*\Delta_{lb} - {}^*\Delta_{le} + {}^*\Delta_{ml} \tag{C.17}$$

Ocean surface layer

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_m = -{}^*\Delta_{ml} - {}^*\Delta_{md} \tag{C.18}$$

Deep sea

$$\left(\frac{d}{dt} + {}^*\lambda\right) {}^*n_d = {}^*\Delta_{md} \tag{C.19}$$

where

$${}^*\Delta_{lu} = -{}^*l_5\,{}^*n_u + {}^*l_6\,{}^*n_l \tag{C.20}$$

$${}^*\Delta_{lb} = -{}^*l_1\,{}^*n_b + {}^*l_2\,{}^*n_l + l'_1 n_b - l'_2 n_l \tag{C.21}$$

$${}^*\Delta_{le} = -{}^*l_3\,{}^*n_e + {}^*l_4\,{}^*n_l + l'_3 n_b - l'_4 n_l \tag{C.22}$$

$${}^*\Delta_{ml} = -{}^*k_3\,{}^*n_l + {}^*k_4\,{}^*n_m + k'_1 n_m \tag{C.23}$$

$${}^*\Delta_{md} = -{}^*k_6\,{}^*n_d + {}^*k_5\,{}^*n_m - k'_2 n_m \tag{C.24}$$

The k's and *k's refer to transfers between reservoirs connected in tandem, and the *l*'s and **l*'s refer to transfers in a branched configuration with the atmosphere (see Fig. 1). The coefficients k'_1, k'_2, l'_1, . . . l'_4 refer to factors that multiply some of the inactive n_i to produce virtual radiocarbon sources of the form $\Sigma\, k' n_i$. These sources lead to readjustments of ^{14}C which arise because of changes in the inactive-carbon content of the reservoirs. The coefficients k'_i and

l_i' are distinguished from k_i and l_i by having the dimensions of k × ^{14}C/(inactive carbon) rather than of k. As defined earlier, γ is the industrial production rate of inactive carbon in the atmosphere, and $^*\gamma$ is a perturbation from steady-state ^{14}C production due to a heliomagnetic effect correlated with sunspots. The latter is evaluated by the relation

$$^*\gamma = {}^*\Gamma_0 \frac{Q_2(S_0 - S)}{Q_1 - Q_2 S_0} \tag{C.25}$$

where S is the number of sunspots with long-term mean value $S_0 = 44.89$, and Q_1 and Q_2 are constants determined by Lingenfelter[41]

$$Q_1 = 2.64$$

$$Q_2 = 0.00297$$

The perturbation equations for inactive carbon have the general form

$$\left(\frac{d}{dt} + \sum_{j\neq i} k_{ij}\right) n_i - \sum_{j\neq i} k_{ji} n_j = \gamma_i \tag{C.26}$$

where the sums are over j = 1 to 6 excluding j = i, and the source term, γ_i, is nonzero only for the lower atmosphere. In matrix notation

$$\mathbf{I}\frac{d\mathbf{n}}{dt} + \mathbf{K}\,\mathbf{n} = \boldsymbol{\gamma} \tag{C.27}$$

For radiocarbon the equations have the same general form except that they include virtual sources. Again in matrix notation

$$\mathbf{I}\left(\frac{d^*\mathbf{n}}{dt} + {}^*\lambda{}^*\mathbf{n}\right) + {}^*\mathbf{K}{}^*\mathbf{n} + \mathbf{K}'\,\mathbf{n} = {}^*\boldsymbol{\gamma} \tag{C.28}$$

when I = the identity matrix and $\mathbf{K}'\mathbf{n}$ denotes the virtual source vector.

Specifically

$$\mathbf{n} = \begin{Bmatrix} n_u \\ n_e \\ n_b \\ n_l \\ n_m \\ n_d \end{Bmatrix} \tag{C.29}$$

$$\boldsymbol{\gamma} = \left\{ \begin{array}{c} 0 \\ 0 \\ 0 \\ \gamma \\ 0 \\ 0 \end{array} \right\} \tag{C.30}$$

$$^{*}\mathrm{n} = \left\{ \begin{array}{c} ^{*}\mathrm{n}_{\mathrm{u}} \\ ^{*}\mathrm{n}_{\mathrm{e}} \\ ^{*}\mathrm{n}_{\mathrm{b}} \\ ^{*}\mathrm{n}_{\mathrm{l}} \\ ^{*}\mathrm{n}_{\mathrm{m}} \\ ^{*}\mathrm{n}_{\mathrm{d}} \end{array} \right\} \tag{C.31}$$

$$^{*}\boldsymbol{\gamma} = \left\{ \begin{array}{c} ^{*}\gamma \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \end{array} \right\} \tag{C.32}$$

$$\mathbf{K} = \left\{ \begin{array}{cccccc} \mathrm{u} & \mathrm{e} & \mathrm{b} & \mathrm{a} & \mathrm{m} & \mathrm{d} \\ l_5 & 0 & 0 & -l_6 & 0 & 0 \\ 0 & l_3 & -l_7 & -l_4 & 0 & 0 \\ 0 & 0 & l_1 & -l_2 & 0 & 0 \\ -l_5 & -l_3 & (-l_1 + l_7) & (l_2 + l_4 + l_6 + \mathrm{k}_3) & -\mathrm{k}_4 & 0 \\ 0 & 0 & 0 & -\mathrm{k}_3 & (\mathrm{k}_4 + \mathrm{k}_5) & \mathrm{k}_6 \\ 0 & 0 & 0 & 0 & -\mathrm{k}_5 & \mathrm{k}_6 \end{array} \right\} \tag{C.33}$$

***K** is identical to **K** except that $^{*}\mathrm{k}_{\mathrm{i}}$ and $^{*}l_{\mathrm{i}}$ replace all k_{i} and l_{i}, and $^{*}l_7$ is zero. **K**$'$ is a matrix of the virtual source coefficients:

$$\mathbf{K}' = \left\{ \begin{array}{cccccc} \mathrm{u} & \mathrm{e} & \mathrm{b} & \mathrm{a} & \mathrm{m} & \mathrm{d} \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -l_3' & 0 & l_4' & 0 & 0 \\ 0 & 0 & -l_1' & l_2' & 0 & 0 \\ 0 & l_3' & l_1' & (-l_2' - l_4') & -\mathrm{k}_1' & 0 \\ 0 & 0 & 0 & 0 & \mathrm{k}_1' & -\mathrm{k}_2' \\ 0 & 0 & 0 & 0 & \mathrm{k}_2' & 0 \end{array} \right\} \tag{C.34}$$

The specific transfer and virtual source coefficients are as follows:

$$l_1 = 0$$

$$l_2 = \frac{\beta F_{b0}}{N_{l0}}$$

$$l_3 = \frac{F_{e0}}{N_{e0}}$$

$$l_4 = \frac{\beta F_{e0}}{N_{l0}}$$

$$l_5 = k_{ul}$$

$$l_6 = \frac{k_{ul} N_{u0}}{N_{l0}}$$

$$l_7 = \frac{F_{e0}}{N_{b0}}$$

$$l_1' = \frac{\alpha_{ab} R_{l0} F_{b0}}{N_{b0}}$$

$$l_2' = \alpha_{ab} R_{l0} \frac{F_{b0}}{N_{l0}} (1 - \beta)$$

$$l_3' = \frac{\alpha_{ab} R_{l0} F_{e0}}{N_{b0}}$$

$$l_4' = \alpha_{ab} R_{l0} \frac{F_{e0}}{N_{l0}} (1 - \beta)$$

$$k_3 = \frac{k_{am} N_{a0}}{N_{l0}}$$

$$k_4 = k_{am} \frac{N_{a0}}{N_{\tilde{m}0}} \xi$$

$$k_5 = \frac{W_d}{W_m} k_{dm}$$

$$\kappa_6 = k_{dm}$$

$$k_1' = \alpha_{ma} k_{am} \frac{N_{a0}}{N_{\tilde{m}0}} R_{m0} \left(\xi - \frac{N_{\tilde{m}0}}{N_{m0}} \frac{\phi}{\phi_0} \right)$$

$$
\begin{aligned}
k_2' &= \alpha_{mg} R_{m0} k_{dm} \left(\frac{N_{d0}}{N_{m0}} - \frac{W_d}{W_m} \right) \\
{}^*l_1 &= \frac{\alpha_{ba} F_{b0}}{N_{b0}} \\
{}^*l_2 &= \frac{\alpha_{ab} F_{b0}}{N_{l0}} \\
{}^*l_3 &= \frac{\alpha_{ba} F_{e0}}{N_{e0}} \\
{}^*l_4 &= \frac{\alpha_{ab} F_{e0}}{N_{l0}} \\
{}^*l_5 &= l_5 \\
{}^*l_6 &= l_6 \\
{}^*k_3 &= \frac{\alpha_{am} k_{am} N_{a0}}{N_{l0}} \\
{}^*k_4 &= \alpha_{ma} k_{am} \frac{N_{a0}}{N_{m0}} \frac{\phi}{\phi_0} \\
{}^*k_5 &= \left[\alpha_{mg} + \frac{N_{m0}}{W_m} \frac{W_d}{N_{d0}} (1 - \alpha_{mg}) \right] \frac{N_{d0}}{N_{m0}} k_{dm} \\
{}^*k_6 &= k_6
\end{aligned} \tag{C.35}
$$

The symbol $N_{\tilde{m}0}$ refers to the total mass of inorganic carbon in the ocean surface layer (= $W_m \Sigma C$). In deriving the expressions for k_1', k_2', ${}^*k_4$, and ${}^*k_5$, we have made the approximation $R_{\tilde{m}} = R_m$. The expression for ϕ, ϕ_0, and ξ are given in Appendix D. ϕ/ϕ_0 is related to ξ by

$$
\frac{\phi}{\phi_0} = \frac{1 + \xi(n_m/N_{\tilde{m}0})}{1 + (n_m/N_{\tilde{m}0})} \tag{C.36}
$$

Thus only ξ or ϕ/ϕ_0 need appear in the coefficient equations; however, it was convenient to use both.

For calculations of radiocarbon, Eqs. C.3 through C.24 were used with constant values of all factors and terms except the source terms γ and ${}^*\gamma$ and the chemical factors ξ and ϕ/ϕ_0. The latter were stepped by the procedure described in Appendix D. The governing equations for transfers involving the land biota were approximated by retaining only the first-order term in the Taylor expansion for F_{lb}, F_{bl}, F_{le}, and F_{el}. Equations for the oceans were similarly approximated by replacing $R_{\tilde{m}}$ with R_m and retaining only first-order terms in the expansions of R_m/R_{m0} and $R_m P_m / R_{m0} P_{m0}$. For the five-reservoir model, Eqs. C.3 and C.14 were ignored, index 1 was replaced by index a, $^*\gamma$ was added to the right-hand side of the equation for the lower atmosphere (Eq. C.17), and Δ_{lu} and $^*\Delta_{lu}$ were set equal to zero. For the three-reservoir model, Eqs. C.4, C.5, C.15, and C.16 were also ignored, and Δ_{lb}, Δ_{le}, $^*\Delta_{le}$, and $^*\Delta_{le}$ were also set equal to zero.

For calculations of inactive carbon, if these included prediction beyond 1969, the following replacements were made in the perturbation equations to restore the expressions for the land biota to their original form as given in Appendix A: Δ_{lb} was replaced by

$$\beta F_{bo}\left(1+\frac{n_b}{N_{bo}}\right)\ln\left(1+\frac{n_l}{N_{lo}}\right) \tag{C.37}$$

and Δ_{le} was replaced by

$$\beta F_{eo}\left(1+\frac{n_b}{N_{bo}}\right)\ln\left(1+\frac{n_l}{N_{lo}}\right)+F_{eo}\left(\frac{n_b}{N_{bo}}-\frac{n_e}{N_{eo}}\right) \tag{C.38}$$

APPENDIX D: EVALUATION OF SURFACE OCEAN EVASION FACTOR

Stoichiometric equilibrium quotients are defined as follows:

$$K_0 = \frac{[CO_2]}{P_m} \tag{D.1}$$

$$K_1 = \frac{[H^+]\,[HCO_3^-]}{[CO_2]} \tag{D.2}$$

$$K_2 = \frac{[H^+]\,[CO_3^{2-}]}{[HCO_3^-]} \tag{D.3}$$

$$K_B = \frac{[H^+]\,[B(OH)_4^-]}{[B(OH)_3]} \tag{D.4}$$

$$K_W = [H^+]\,[OH^-] \tag{D.5}$$

where brackets denote concentrations in moles per liter of seawater.

The quotients were evaluated for average ocean surface water with temperature 19.59°C (T = 292.75°K) and chlorinity (Cl) 19.24 per mil. Equations for the equilibrium quotients in seawater are[5]

$$-\log(K_0) = \frac{-2622.38}{T} + 15.5873 - 0.0178471T + 0.0117950\ \mathrm{Cl} - (2.77676 \times 10^{-5})\ \mathrm{Cl}\ T \qquad \text{(D.6)}$$

$$-\log(K_1) = \frac{3523.46}{T} - 15.6500 + 0.034153T - 0.074709\ (\mathrm{Cl})^{1/2} - 0.0023483\ \mathrm{Cl} \qquad \text{(D.7)}$$

$$-\log(K_2) = \frac{2902.39}{T} - 6.4980 + 0.023790T - 0.45322\ (\mathrm{Cl})^{1/2} + 0.035226\ \mathrm{Cl} \qquad \text{(D.8)}$$

$$-\log(K_B) = \frac{2291.90}{T} - 3.3850 + 0.01756T - 0.32051\ (\mathrm{Cl})^{1/3} \qquad \text{(D.9)}$$

K_W was interpolated from a table of Harvey.[45] By a widely accepted convention $[H^+]$ was replaced in the defining Eqs. D.2 to D.5 by a thermodynamic activity whose negative logarithm is denoted by the symbol pH. This replacement has a negligible effect on the calculations discussed in this paper, and we have assumed $\mathrm{pH} = -\log[H^+]$.

The values of the equilibrium quotients for average ocean surface water are $K_0 = 0.03347$, $K_1 = 9.747 \times 10^{-7}$, $K_2 = 8.501 \times 10^{-10}$, $K_B = 1.881 \times 10^{-9}$, and $K_W = 6.463 \times 10^{-15}$. Other properties of average ocean surface water are: alkalinity (A) = 2.435 meq/liter, initial pH = 8.271, total boron concentration $(\Sigma B) = 0.409$ millimole/liter, and initial total inorganic-carbon concentration = 2.057 millimole/liter. The chemical properties of average ocean water are as derived by Keeling.[5]

The equation for total inorganic carbon concentration is

$$\Sigma C = [CO_2] + [HCO_3^-] + [CO_3^{2-}] = \frac{P_m}{\phi} \qquad \text{(D.10)}$$

where

$$\frac{1}{\phi} = K_0 \left(1 + \frac{K_1}{[H^+]} + \frac{K_1 K_2}{[H^+]^2}\right) \qquad \text{(D.11)}$$

ϕ_0 in Appendix C is ϕ evaluated at the initial hydrogen-ion concentration. The variation of ϕ with isotopic mass (which enters the perturbation equations only as the ratio of $^*\phi\phi_0/^*\phi_0\phi$ where $^*\phi$ and $^*\phi_0$ denote the radioisotope equivalents of ϕ and ϕ_0) is too small to justify distinguishing between inactive and radiocarbon.[5]

The equations for total boron and alkalinity are

$$\Sigma B = [B(OH)_3] + [B(OH)_4^-] = \left(1 + \frac{[H^+]}{K_B}\right) [B(OH)_4^-] \tag{D.12}$$

$$A = [HCO_3^-] + 2[CO_3^{2-}] + [B(OH)_4^-] + [OH^-] - [H^+] \tag{D.13}$$

Consequently

$$A = \frac{K_1/[H^+] + 2K_1K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2} \Sigma C + \frac{\Sigma B}{1 + [H^+]/K_B} + \frac{K_W}{[H^+]} - [H^+] \tag{D.14}$$

To calculate the evasion factor

$$\xi = \left[\frac{(P_m - P_{m0})/P_{m0}}{(\Sigma C - \Sigma C_0)/\Sigma C_0}\right]_{\text{constant } A}$$

Eq. D.14 for A is rearranged as a polynomial in $[H^+]$,

$$\sum_{n=0}^{5} D_n [H^+]^n = 0$$

where

$$\begin{aligned}
D_0 &= -K_1K_2K_BK_W \\
D_1 &= [(A - 2\Sigma C - \Sigma B)K_2K_B - (K_2 + K_B)K_W]K_1 \\
D_2 &= [(A - 2\Sigma C + K_B)K_2 + (A - \Sigma C - \Sigma B)K_B]K_1 - (K_1 + K_B)K_W \\
D_3 &= (A - \Sigma B + K_1)K_B + (A - \Sigma C + K_2)K_1 - K_W \\
D_4 &= A + K_1 + K_B \\
D_5 &= 1
\end{aligned} \tag{D.15}$$

The polynomial was iteratively solved by Newton's method for a new value of $[H^+]$ corresponding to the new total inorganic carbon concentration $\Sigma C_0 + \Delta\Sigma C$. The iteration step,

$$[H^+]_{i+1} = [H^+]_i - \frac{\sum_{n=0}^{5} D_n [H^+]_i^n}{\sum_{n=1}^{5} nD_n [H^+]_i^{n-1}} \tag{D.16}$$

where i refers to the iteration, was repeated until the magnitude

$$\left|\frac{[H^+]_{i+1} - [H^+]_i}{[H^+]_i}\right|$$

was less than 10^{-10}. A new value of P_m was then calculated, and ξ and φ were evaluated.

APPENDIX E: NUMERICAL VALUES OF MODEL PARAMETERS

Unless otherwise indicated, all numerical values, together with their references, are as given by Keeling.[5]

Parameter	**Definition**
p_{CO_2}	Preindustrial CO_2 partial pressure in atmosphere expressed as mixing ratio
M_a	Total atmospheric mass excluding water vapor
W_s	Total ocean volume
C_d	Total carbon concentration in deep ocean
$C_{\tilde{m}}$	Inorganic-carbon concentration in surface ocean
C_{org}	Dissolved organic-carbon concentration in surface ocean

Parameter	**Value or Equation for Calculating Value**
p_{CO_2}	290 ppM (parts per million of CO_2 relative to dry air)
M_a	5119×10^{18} g of dry air
W_s	1370×10^{18} liters
C_d	0.0284 g/liter
$C_{\tilde{m}}$	(12.011 g/mole)(0.002057 mole/liter)
C_{org}	0.001 g/liter
N_{ao}	$[(12.011 \text{ g/mole})/(28.946 \text{ g/mole})]\, p_{CO_2} M_a = 6.156 \times 10^{18}$ g of C
N_{uo}	$0.15 N_{ao}$ (as given by Machta[39])
N_{lo}	$N_{ao} - N_{uo}$
N_{mo}/N_{ao}	Variable parameter
N_{mo}	$(N_{mo}/N_{ao})N_{ao}$
W_m	$N_{mo}/(C_{\tilde{m}} + C_{org})$
$N_{\tilde{m}o}$	$C_{\tilde{m}} W_m$
W_d	$W_s - W_m$
N_{do}	$C_d W_d$
α_{ab}	0.964
α_{ba}	1.000
α_{am}	0.972
α_{ma}	0.955
α_{mg}	0.966
$^*\lambda$	1/8267 year^{-1}
k_{ul}	$\frac{1}{2}$ year^{-1} (as given by Machta[39])
k_{am}	Variable parameter
k_{dm}	Variable parameter
F_{bo}	0.026×10^{18} g/year
F_{eo}	0.030×10^{18} g/year
β	Variable parameter
N_{eo}	0.075×10^{18} g of C $= 0.122\, N_{ao}$
N_{bo}	1.56×10^{18} g of C $= 2.534\, N_{ao}$

APPENDIX F: DERIVATION OF ANNUAL SUNSPOT NUMBERS FOR THE YEARS 1500 to 1699

Sunspot numbers from the Zurich Observatory, as calculated by Wolf and his successors, are given by Abetti[46] for the period 1749 to 1961. Schove[47] gives comparable numbers for 1700 to 1749 and has extended the record back to 649 by estimating the years of sunspot maximums and the intensity of the maximums from records of sunspots seen with the naked eye and displays of northern lights. To obtain annual numbers before 1700, we have calculated an average normalized sunspot cycle from the data after 1749. Then, by adjusting this curve to the years and intensities of maximum activity from 1500 to 1699, we have filled in sunspot numbers for the intervening years.

Twenty sunspot maximums occurred between 1750 and 1960. The number of years between maximums varied from 7 to 16. To obtain a valid average cycle, we projected the record forward and backward from each maximum and found the average number of sunspots for equidistant years. If the number of intervening years was even, we split the record into equal numbers of years forward and backward, and, if odd, we included one more year forward. Beyond 6 years in either direction, too few instances occurred to give a statistically good average.

The number of sunspots for each year of the average cycle, expressed as a percentage of the average maximum, is as follows:

Year relative to maximum	Number of spots, % of maximum
−6	0.05
−5	0.08
−4	0.13
−3	0.20
−2	0.42
−1	0.74
0	1.00
1	0.85
2	0.69
3	0.51
4	0.34
5	0.24
6	0.16

To estimate the annual record before 1700, we multiplied the percent values of the average cycle by the appropriate maximum, and used this value to project each cycle forward and backward in the same manner as in constructing the average cycle. On three occasions, 1512, 1565, and 1667, the average cycle was too short to give a value; we obtained values of 6, 12, and 3 sunspots, respectively, by interpolation. The reconstructed record is plotted in Fig. 9.

DISCUSSION BY ATTENDEES

Livingstone: Can you give us an estimate of the proportions of the ocean surface water in which the p_{CO_2} exceeds that of the air over it, and that in which p_{CO_2} is less?

Bacastow: Generally, in the tropics where the water is warm, CO_2 is released to the atmosphere; in polar regions where the water is colder, CO_2 is absorbed.

ATMOSPHERIC CARBON MONOXIDE

RICHARD D. CADLE
National Center for Atmospheric Research,* Boulder, Colorado

ABSTRACT

Carbon monoxide (CO) is a colorless, odorless gas produced principally by combustion of organic substances. It is probably also produced by bacterial action on land and in the oceans. Concentrations in the "natural" troposphere average 0.1 to 0.2 ppMv (parts per million by volume). In smoggy city air 40 ppMv is common. The mechanisms of removal of CO from the atmosphere are not well known but seem to include chemical reactions in both the troposphere and stratosphere and bacterial action at Earth's surface.

Carbon monoxide (CO) is a colorless, tasteless, and nearly odorless gas. It is slightly soluble in water, about 2.5 ml in 100 ml of water at 19°C and 760 torrs. Its melting point is −199°C, and its boiling point is −191.5°C. It has been considered "inactive" chemically with respect to most substances unless heated considerably above 300°K or in the presence of a suitable catalyst.

The toxicity of CO to man results from its ability to combine with the hemoglobin of the blood, preventing the hemoglobin from combining with oxygen. The reaction is reversible, but the affinity of hemoglobin for CO is more than 200 times that for oxygen. Early symptoms are headache and nausea. Unconsciousness is produced in about an hour by 0.2 vol.% CO in air; 1.0 vol.% is reported to be rapidly fatal. Much less is known about chronic effects of CO, but long-term exposure of animals to CO seems to produce morphological changes in the heart and brain[1] and may cause increased hemoglobin levels.

Plants are relatively insensitive to CO. Alterations of plant characteristics have been reported by exposures[1] exceeding 10,000 ppMv CO.

Carbon monoxide emission is one of the oldest problems of air pollution. Poisoning by CO apparently has been reported in Greek and Roman literature.[1]

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but there has been little interest in it as a pollutant except when CO concentrations were high enough to produce acute physiological effects. Interest has been stimulated recently by evidence that there are chronic as well as acute physiological effects and by recognition that CO takes part in complex chemical reactions in air. Work has been stimulated by development of analytical techniques capable of resolving CO concentrations in the range of fractions of a part per million in air.

SOURCES OF CO

Until recently it seemed well established that man's activities were the main sources of CO in the atmosphere. Now there is growing evidence that the oceans are also an important source. According to Robinson and Robbins,[2] the total worldwide CO emission from combustion is 285×10^6 tons or about 2.6×10^{14} g. Automobiles are the major source, accounting for about 68% of the total produced by combustion. This value was based on the assumption that 2.91 lb of CO are produced per gallon of gasoline and that the annual worldwide gasoline production in 1966 was 379×10^6 tons. Other important sources by man are fuel combustion in stationary sources, industrial processes, and solid-waste disposal. Detailed estimates by source category are given in the literature.[1,2]

The chemical reactions that occur in photochemical smog produce CO. Results of investigations of such production have been summarized by Altshuller and Bufalini.[3] The yields for most of the olefins and aromatic hydrocarbons reacted in "synthetic" smog are about 0.2 mole of CO per mole of hydrocarbon reacted. If we assume that about 2% of the gasoline burned in an automobile is emitted as unburned hydrocarbons in the exhaust, that half of this unburned gasoline takes part in photochemical reactions, and that the average molecular weight of the gasoline is 120, the yield of CO is 10^{-4} times the amount of gasoline consumed by automobiles. And if we assume, as was done earlier, that the worldwide annual production of gasoline is 379×10^6 tons, the yield of CO formed photochemically from unburned gasoline would be 379×10^2 tons, an insignificant figure compared with the amounts produced by combustion.

Man's contribution to the CO content of the atmosphere is much greater in the Northern than in the Southern Hemisphere because 95% of world gasoline consumption occurs in the Northern Hemisphere.

Perhaps the most obvious natural sources of CO are forest, brush, and grass fires. Robinson and Robbins[2] estimated an annual worldwide emission from forest fires of 11×10^6 tons.

Recent research on the oceans as a source of CO has been reviewed by Seiler and Junge[4] and by Junge, Seiler, and Warneck.[5] Compelling evidence was obtained by Swinnerton, Linnenbom, and Check[6] that surface waters of the western Atlantic Ocean are supersaturated with CO. Swinnerton, Linnenbom, and Lamontague[7] found at two places in the Atlantic that the CO concentration in water varied daily, indicating a biotic origin. Robinson and Robbins[2,8] analyzed near-surface air over the Pacific Ocean during several cruises. They observed CO concentrations in the Southern Hemisphere about one-half to one-third those in the mid-latitudes of the Northern Hemisphere and also observed weak diurnal cycles, with lower concentrations occurring in early afternoon and higher concentrations at night. These results seem to indicate that the oceans are a CO source. Seiler and Junge[9] measured CO concentrations near the tropopause and found a decrease with increasing altitude above the tropopause, but their tropospheric measurements failed to show the differences in CO concentrations between the Northern and Southern Hemispheres reported by Robinson and Robbins.[2] Later they[4] also found that seawater is supersaturated with CO. Junge et al.[5] estimated the amount of CO released from the oceans to be about 29% of the total of man's emissions. Swinnerton et al.[7] earlier had obtained a figure of 5%. The oceans appear to be an important biogenic source of CO.

Vegetation may also contribute to the CO content of the atmosphere, but little is known about this possibility. Wilks[10] found that green plants grown in a closed, illuminated system (plastic bags) emit small amounts of CO. Also, finely divided powder and chlorophyll extracts of green plants, when illuminated in an atmosphere of oxygen and water vapor, emitted both CO and aldehydes.

Volcanic action is another natural source of CO. A very crude idea of the average annual emission can be obtained by making the entirely unsubstantiated assumption that all volcanoes emit CO in the same amounts relative to the amounts of lava (including pyroclastic materials). Then, using the same approach as was used by Kellogg et al.[11] to estimate annual SO_2 emissions and using the data of Shepherd[12] for the composition of Kilauea volcano (Hawaii) gases, we see that the annual volcanic emission of CO is about 7.5×10^4 tons. This quantity is insignificant compared with the emissions from combustion.

Another possible, but highly speculative, natural source of CO is the sequence of chemical reactions that produce CO in photochemical smog but involve the organic vapors (essential oils) evolved by plants and naturally produced oxides of nitrogen. Such vapors are emitted by many species of plants, and hundreds of organic compounds have been identified in essential oils. Such photochemical reactions may be responsible for much natural haze, such as that which forms over the jungles of Colombia. Rasmussen and Went[13] estimated the worldwide emission of such vapors to be 4.4×10^8 tons/year, but Ripperton, White, and Jeffries[14] suggest that this estimate may be too low by a factor of 2 to 10. If we assume that the annual emission of such vapors is 10^9 tons/year, that the molar yield of CO is 0.2, that (as just mentioned) half of the essential oils take part in photochemical reactions, and that the average molecular weight of the essential oils is 140, then the annual production from these reactions is 20×10^6 tons.

Swinnerton, Lamontague, and Linnenbom[15] found concentrations of CO in rainwater collected at widely diverse locations corresponding to up to 200-fold supersaturation relative to the partial pressure of CO in the atmosphere. They concluded that the results indicated a natural source of CO that had not previously been considered. They tentatively attributed the production to the photochemical oxidation of organic matter or to the dissociation of carbon dioxide induced by electrical discharges, or to both. No attempt was made to estimate the annual production.

One other suggestion relating to sources of atmospheric CO should be mentioned. Weinstock and Niki,[16] on the basis of steady-state equations for stable CO and for radioactive CO in the troposphere, concluded that CO is produced in the troposphere at a rate of 5×10^{15} g/year, "some 25 times greater than the rate of carbon monoxide production from combustion." They suggest that the source is the sequence of reactions

$$O_3 + h\upsilon \rightarrow O_2 + O(^1D) \tag{1}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{2}$$

$$OH + CH_4 \rightarrow H_2O + CH_3 \tag{3}$$

followed by the oxidation of CH_3 to form CO.

The above-mentioned production estimates are summarized in Table 1.

TABLE 1

ESTIMATES FROM VARIOUS SOURCES OF THE ANNUAL PRODUCTION OF CARBON MONOXIDE

Man's activities		Natural sources	
Activity	CO yield, 10^6 tons/year	Source	CO yield, 10^6 tons/year
Automobiles	195	Forest fires	11
Combustion other than automobiles	90	Oceans	83
Photochemical production	0.04	Photochemical production from essential oils	20
		Volcanoes	0.075
		Photochemical production from methane*	5000

*Suggestion of Weinstock and Niki.[16]

CONCENTRATIONS

Numerous studies have been made of CO concentrations in the ambient troposphere, and the results have been discussed in the reviews mentioned in the preceding paragraphs.[2,4,5] The average concentration is about 0.1 to 0.2 ppMv, but there is a large variation about this mean. For example, Robinson and Robbins[2] obtained values at Inge Lehmann station in Greenland varying from about 0.1 to 0.7 ppMv. Measurements by Seiler and Junge[4] in the vicinity of the tropopause showed that a rapid decrease in CO concentration with increasing altitude occurs in the lower stratosphere.

In polluted atmospheres, such as city smog, the concentrations are of course very much higher and extremely variable. A typical concentration would be 40 ppMv.

RESIDENCE TIMES

Residence times for an atmospheric species can be defined in at least two ways. One is the mean or average lifetime that can be obtained by dividing the total amount in the atmosphere by the rate of addition to the atmosphere. Another definition involves the so-called tau value [thus: $\tau(\mathrm{CO})$], which is the atmospheric concentration divided by the removal rate. For many processes this is the time required to decrease the concentration to 1/e of the original value.

Junge, Seiler, and Warneck[5] suggest a value of 1 year for the average residence time and that there must be differences between the tropospheric lifetimes of ^{14}CO and ^{12}CO. Weinstock and Niki[16] estimated a residence time, defined as the reciprocal of the first-order rate constant for CO removal, of 0.1 year. They assumed that the rate constants for ^{12}CO and ^{14}CO are identical.

CO-REMOVAL PROCESSES

Our knowledge of the processes for the removal of CO from the atmosphere is at least as uncertain as our knowledge of the sources and the residence time. Pressman and Warneck[17] suggest that chemical reactions in the stratosphere contribute significantly, but only partially, to the overall removal of CO from the atmosphere. They suggest that the most important removal process is

$$OH + CO \rightarrow CO_2 + H \qquad (4)$$

Another reaction that must remove some CO in the stratosphere is

$$O(^3P) + CO + M \rightarrow CO_2 + M \qquad (5)$$

Data for this reaction are conflicting, but recent work suggests that the rate constant is much smaller than earlier studies indicated. Using the rate constant recently obtained by Simonaitis and Heicklen,[18] we can readily show that $\tau(CO)$ must be about 100 years at 20 km altitude and about 10 years at 60 km altitude by reaction 5, much too small to be important. The reaction

$$O(^1D) + CO \rightarrow \text{products} \tag{6}$$

seems to lead to quenching of the $O(^1D)$ to the electronic ground state instead of to chemical reaction.[19]

Just as Weinstock and Niki[16] invoked reactions 1, 2, and 3 for the formation of CO in the troposphere, they invoked reactions 1, 2, and 4 for destruction in the troposphere. The reaction of $O(^3P)$ with aldehydes produces OH radicals in smog,[20-22] and this reaction may be followed by reaction 4. Then the following reactions occur:

$$H + O_2 + M \rightarrow HO_2 + M \tag{7}$$

and

$$HO_2 + NO \rightarrow OH + NO_2 \tag{8}$$

Other radicals may play a similar role:[23]

$$CO + RO \rightarrow CO_2 + R \tag{9}$$

$$R + O_2 \rightarrow RO_2 \tag{10}$$

$$RO_2 + NO \rightarrow RO + NO_2 \tag{11}$$

where R is the organic fraction of the radical.

However, Kummler, Bortner, and Jaffe[24] state that it is highly unlikely that homogeneous gas-phase kinetics at ground level can be an appreciable sink for CO, that possibly a heterogeneous chemistry is involved, but that it is more probable that a biological sink is required to convert CO to CO_2. Such a sink could involve both land surfaces and oceans, and it is possible that at certain times and places the oceans serve as a source of CO, whereas at other times they serve as a sink.

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DISCUSSION BY ATTENDEES

Stevens: We have been working on the carbon and oxygen isotopic composition of carbon monoxide in unpolluted atmospheres and find the predominant species has a light oxygen isotopic composition that is quite different from the isotopic composition of engine-produced carbon monoxide. The estimated production rate is 10 to 30 times greater than annual engine emissions, and this estimate agrees with Weinstock's value. We also find a burst of carbon monoxide in the autumn which may be from the degradation of chlorophyll at the end of the growing season.

Muckerman: A factor that complicates Reaction No. 4 ($OH + CO \rightarrow CO_2 + H$) is the possibility that the intermediate formic acid radical (COOH) is stable. This radical has been isolated in a solid matrix and characterized by IR spectroscopy by A. Milligan. Molecular orbital calculations by M. Newton at Brookhaven National Laboratory predict that COOH is *more* stable than $CO_2 + H$. It seems to me that, at pressures of about an atmosphere, the COOH intermediate in reaction 4 could be stabilized and then undergo a chemistry of its own. None of the various experimental studies of the kinetics of Reaction No. 4 has reported this COOH product, but those experiments which have analyzed products have been carried out at pressures where one would not expect the necessary collisional stabilization.

Cadle: It has been the history of gas phase rate constants that, as more sophisticated work is done, rate constants tend to be lowered. The reason often is that the early studies have overlooked such things as hetergeneous reactions on the walls.

METHANE IN THE ATMOSPHERE

DIETER H. EHHALT
National Center for Atmospheric Research,* Boulder, Colorado

ABSTRACT

The atmospheric cycle of CH_4 is described. Most of the CH_4 released to the atmosphere is of recent biologic origin. Carbon-14 analyses show that, at most, 20% of the atmospheric CH_4 is released by fossil sources. The estimated total annual production of CH_4 is between 6.5×10^{14} and 19×10^{14} g/year. The destruction of CH_4 takes place mainly in the troposphere, most probably through the reaction $CH_4 + OH \rightarrow CH_3 + H_2O$. Only about 10% of the CH_4 is destroyed in the stratosphere. The total destruction rate is estimated to be 3×10^{15} g/year. Apparently the CH_4 cycle contributes about 1% to the atmospheric carbon cycle. The average volume mixing ratio in the troposphere is 1.41 ppM, which corresponds to a total amount of 4×10^{15} g of CH_4 present in the atmosphere. Thus the turnover times of atmospheric CH_4 range from 1 to 6 years. The vertical profiles of CH_4 in the troposphere show no large systematic gradients. In the stratosphere the CH_4 mixing ratio decreases with altitude, reaching 0.25 ppM at 50 km. Finally, the isotopic composition of atmospheric CH_4 and its sources are discussed briefly.

The presence of methane in the earth's atmosphere was discovered by Migeotte.[1] It was identified by its infrared absorption band in the solar spectrum. The early optical measurements indicated a uniform distribution of CH_4 throughout the atmosphere, with an average volume concentration of about 2 ppM. Subsequent measurements[2] lowered this value to 1.5 ppM and then to 1.4 ppM. Our own measurements using gas chromatography give an average of 1.41 ppM for the troposphere and indicate a decrease in concentration in the stratosphere.[3] Our measurements also show that the CH_4 concentration fluctuates greatly even in tropospheric profiles.[4]

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Methane is classified as a long-lived pollutant. Initially the atmospheric lifetime of methane was estimated to be about 100 years. More recently the lifetime has been estimated to be only a few years.

Interest in the CH_4 cycle, particularly in its stratospheric branch, has recently been stimulated by two developments. The first of these was the realization that the oxidation of CH_4 in the stratosphere adds significant amounts of water to the water cycle in the middle and upper stratosphere. It is estimated that about 50% of the water vapor in that region comes from the oxidation of CH_4. This additional water vapor influences the earth's radiation balance causing a slight increase of the temperature at the earth's surface and a decrease of the stratospheric temperature.[5] The added water vapor is even more important for the stratospheric chemistry because it and the free radicals, OH and HO_2, derived from it interact with the ozone. The net effect is a reduction of the O_3 present in the stratosphere. Thus the CH_4 produced in the troposphere influences the stratospheric environment. This has led to the speculation that anthropogenic production of CH_4, which seems to be increasing, may contribute to changes in the stratospheric environment.

The second development that has renewed interest in the CH_4 cycle involves the oxidation process of CH_4 in the troposphere. It was theorized recently that the oxidation of CH_4 leads to the formation of CO as an intermediate step.[6] This process may very well be the major source of CO. Thus the CH_4 cycle is coupled closely to the atmospheric CO cycle and, incidentally, is also coupled to the atmospheric H_2 cycle. Neither the CO cycle nor the H_2 cycle can be understood quantitatively without understanding the CH_4 cycle. Published measurements over the past 10 years showed that the average tropospheric CH_4 concentration is practically constant with time. Apparently the CH_4 cycle is in a steady state, and the balance is solely determined by the sources and sinks of CH_4.

SOURCES OF ATMOSPHERIC CH_4

It is generally agreed that CH_4 is too complicated a molecule to be synthesized within the atmosphere and that it is released mainly at the earth's surface. Even before detailed estimates of the CH_4 sources were available, it was known that most of the atmospheric CH_4 must be produced by anaerobic decomposition of recent organic matter. This information was provided by the measurement of the radiocarbon content in atmospheric CH_4. Any CH_4 derived from "recent," i.e., recently alive, organic material has a ^{14}C content very close to that of recent wood. In contrast, CH_4 derived from fossil fuels or volcanic activity contains essentially no ^{14}C. The fuel deposits are so old that the originally present ^{14}C has decayed. Several ^{14}C analyses of atmospheric CH_4, mostly made by Libby,[7] are available and are summarized in Table 1. Most of these samples were collected before the atmosphere was contaminated with the

^{14}C from nuclear explosions and should represent the natural ^{14}C level in CH_4. The average ^{14}C content is 80% of that of recent wood, which indicates that 80% of the CH_4 is of recent biologic origin and 20% is "dead" CH_4. This 20% represents an upper limit. The measured CH_4 samples have been provided by air-liquefaction plants, which are usually situated in heavily industrialized areas. Hence these samples might have been subjected to local contamination by industrial (dead) CH_4.

TABLE 1

^{14}C CONTENT OF ATMOSPHERIC CH_4 SAMPLES

Sample origin	Collection date	^{14}C content, % standard wood	Ref.
Tonawanda, N. Y.	October 1950	102 ± 3	7
Wembley, England	December 1949	75 ± 2	7
Wembley, England	April 1950	69 ± 2	7
Gary, Ind.	January 1960	75.2 ± 0.5	39
Average		80 ± 15	

The fact that most of the atmospheric CH_4 must be produced by the anaerobic decay of recent organic matter simplifies considerably the search for its sources. One can concentrate on the biologic sources. Table 2 lists the known biologic sources and their annual production. The average source strengths and the total areas of the sources are also included. Clearly, humid or marshy areas that provide anaerobic conditions constitute the major sources. There the source strength can be as high as 210 tons km^{-2} $year^{-1}$ or 210 g m^{-2} $year^{-1}$. This is nearly 10% of the annual net production of dry organic matter in a swamp in temperate latitudes, which is 2500 g m^{-2} $year^{-1}$. All other sources are considerably weaker. By multiplying the source strengths with the global area, we obtain the annual CH_4 production of the different ecological systems. Also on a global scale, marshy areas are of major importance. There are a few discrepancies in Table 2 which need to be discussed. First, we have two estimates for CH_4 production in the digestive tract of animals. Hutchinson's estimate[8] is 25 years older, and Singer's larger estimate[9] reflects mainly an increase in cattle population (1.5% per year). The difference between the two estimates for the production of swamps is more serious. Robinson and Robbins[10] assumed that swamps and paddy fields have the same production rate per unit area. A rather careful estimate by Koyama[11] for the CH_4 production rate of paddy fields is based on the mean CH_4 productivity of paddy soils and the mean depth and temperature of the paddy fields (Table 2). However, extrapolation of the production rate per unit area in paddy fields to that in swamps implies that the average depth, temperature, and chemical character of marshy and paddy soils are the same. This is unlikely, and one would like to have an independent value

TABLE 2

SOURCES OF ATMOSPHERIC CH_4*

Source	Average source strength, $g\ km^{-2}\ year^{-1}$	Total area, km^2	Annual production, g/year	Refs.
Paddy fields	2.1×10^8	9.2×10^5	1.9×10^{14}	11
Swamps	2.1×10^8 †	2.6×10^6 ‡	5.4×10^{14}	10
	1.05×10^8 §	2.6×10^6 ‡	2.7×10^{14}	
Enteric fermentation of animals			4.5×10^{13}	8
			7.3×10^{13}	9
Forests	0.9×10^4	4.4×10^7	4×10^{11}	11
Upland fields, grassland, brushland, cultivated areas	4.4×10^5	3×10^7	1×10^{13}	11
Humid tropical areas	2.1×10^7 ¶	2.9×10^7	6.1×10^{14}	10
Total biogenic production rate			5.2×10^{14} to 15.1×10^{14}	
Coal fields			2×10^{13}	11
Amount of CH_4 in the atmosphere (based on 1.41 ppM mixing ratio)			4.0×10^{15} g	
Annual output of CH_4 from natural-gas wells in 1965			5.2×10^{14}	
Annual production of dry organic matter			1.65×10^{17}	25

*The amount of CH_4 in the atmosphere, the production by natural-gas wells and the annual production of dry plant material are given in the last three lines for comparison.

†Average source strength taken to be equal to Koyama's (Ref. 11) value for paddy soils.

‡Area estimated by Twenhofel (Ref. 26).

§Source strength based on average production of CH_4 by Maryland marshes (Refs. 12 and 27).

¶Source strength assumed to be 10% of Koyama's (Ref. 11) value for paddy soils.

for the source strength of marshes. Therefore I have added the CH_4 productivity obtained by Conger[12] for Maryland marshes. It is only half the value for paddy soils, which is in fair agreement. If we assume this value to be more representative of the global average for swamps, we obtain an annual CH_4 production of only 2.7×10^{14} g/year. The correct value probably lies somewhere between the two estimates given in Table 2.

Finally, Robinson and Robbins,[10] in their data for humid tropical areas (listed separately from their data for swamps in Table 2), assumed a source strength of 0.1 of that of the paddy fields. Since the area is large, the resulting annual production is quite large, 6.1×10^{14} g/year. One can argue, however, that the production by humid tropical areas is already included in Koyama's[11] original estimates, given in lines 6 and 7 of Table 2, because the tropical areas are either forests, grass, brushland, or cultivated areas. Koyama's[11] values of annual production by these sources, however, are much smaller than the value assumed by Robinson and Robbins.[10]

If we, for the moment, accept all these figures and combine all the lower estimates and then all the higher estimates for the various sources, we obtain 5.2×10^{14} g/year as a lower limit and 15.1×10^{14} g/year as an upper limit for the "known" biogenic production of CH_4.

There are certainly more biogenic sources of atmospheric CH_4 which might be of global importance, but their strength has not yet been estimated. One example is the ocean, especially coastal waters. It has been shown by Swinnerton and Linnenbom[13] that ocean water contains dissolved CH_4 and is probably slightly supersaturated with respect to the partial pressure of atmospheric CH_4. In addition, there are a few vertical profiles that show an increase in dissolved CH_4 with depth in Gulf of Mexico water and also in the open ocean.[13] At present there are not sufficient data to allow an estimate of oceanic production. Considering the vast area, however, this source might be important.

Of course there are other, nonbiologic sources, but geothermal areas, coal fields, gas wells, industrial areas, and internal combustion engines constitute only minor, although highly localized, sources. We may lump these sources of ^{14}C-free (dead) CH_4 together and assume, on the basis of the ^{14}C content of atmospheric CH_4, that their production is at most 25% of the biogenic production. The total annual CH_4 production then lies between 6.5×10^{14} and 19×10^{14} g/year.

It is interesting to compare the total biogenic production of CH_4 to the figures listed in the last three lines of Table 2. From this comparison we find that the release of biogenic CH_4 to the atmosphere equals or exceeds the annual production of CH_4 from natural-gas wells. We further find that the released CH_4 is about 1% of the annual production of dry organic matter. Since the energy content of CH_4 is about three times that of cellulose, about 1 to 3% of the solar energy fixed by photosynthesis is lost to the atmosphere as CH_4 and escapes the biologic food chain. Finally, by comparing the biogenic production rate of CH_4 to the total amount of CH_4 present in the atmosphere, we obtain a CH_4 turnover time of 2.6 to 8 years (see Table 4).

SINKS OF ATMOSPHERIC CH_4

Since the CH_4 cycle is in steady state, the production of CH_4 has to be matched by its destruction. It was well known that CH_4 reacts with atomic oxygen, especially with the excited O^1D atom, and with the OH radical. However, it was assumed that the concentration of OH (and O) was too low in the troposphere to destroy CH_4 at any significant rate. These reactions were thought to be important only in the stratosphere. This view has changed recently after Levy[14] proposed a reaction cycle that maintains the OH concentration at a tropospheric average[6] of about 2.5×10^6 cm^{-3}. With such an OH concentration, the destruction of CH_4 in the troposphere becomes very important. Although only the first step in the oxidation of CH_4 is of importance here, the whole sequence is of interest because CO and H_2 appear as intermediate products. Thus the CH_4 cycle is coupled to the CO and H_2 cycle.

$$CH_4 + OH \rightarrow CH_3 + H_2O \tag{1}$$

$$CH_3 + O_2 \rightarrow CH_3O_2 \tag{2}$$

$$CH_3O_2 + NO \rightarrow CH_3O + NO_2 \tag{3}$$

$$CH_3O + O_2 \rightarrow HCOH + HO_2 \tag{4}$$

$$HCHO \begin{cases} + OH \rightarrow CHO + H_2O \\ + h\nu \rightarrow H_2 + CO \\ + h\nu \rightarrow CHO + H \end{cases} \tag{5}$$

$$CHO + O_2 \rightarrow CO + HO_2 \tag{6}$$

$$CO + OH \rightarrow CO_2 + H \tag{7}$$

The rate[15] of reaction 1 is 9×10^{-15} cm^3 $molecule^{-1}$ sec^{-1} at 300°K. From this and the OH concentration, we obtain a tropospheric turnover time of 1.4 years. The corresponding destruction rate is 2.9×10^{15} g/year (see Table 3). This reaction rate may be an overestimate of about 30% because the rate of reaction 1 decreases with temperature[15] and the mean temperature in the troposphere is less than 300°K. However, in view of the uncertainties in the tropospheric concentration of OH, such a refinement seems unnecessary at present.

This reaction scheme works in the stratosphere as well, and the stratosphere also acts as a sink for CH_4. This was already confirmed experimentally when the first stratospheric CH_4 profiles showed a large decrease in the CH_4 mixing ratio up to 23 km[3]. Figure 1 gives another example of a stratospheric CH_4 profile extending the measured decrease to an altitude of 50 km, where the CH_4 mixing ratio[16] drops to 0.25 ppM.

The losses of CH_4 to the stratosphere are determined by the rate of transport from the troposphere into the stratosphere. There are two processes to be considered. The first is the Hadley cell circulation that penetrates into the lower tropical stratosphere. Newell[17] estimated that the mean rising motion in the tropics has a velocity of about 0.02 cm/sec. From this he deduced a flux of 2.4×10^{12} g air/sec into the stratosphere. This flux leaves the stratosphere at

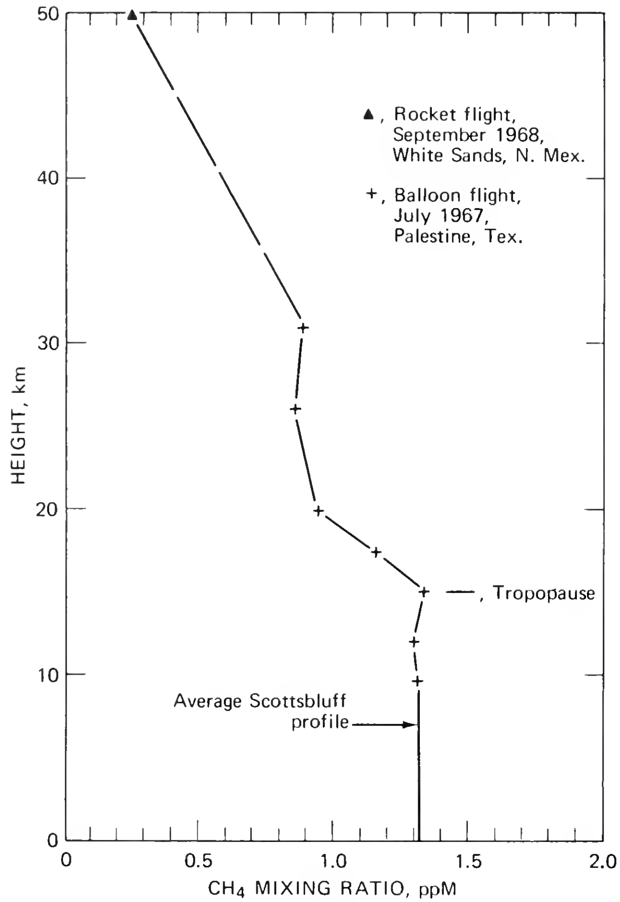

Fig. 1 Vertical profile of the CH_4 volume mixing ratio in the stratosphere. The balloon data[18] are supplemented by the results of a rocket flight which collected an integrated sample at altitudes between 44 and 62 km. The weighted mean altitude[16] of this sample is 50 km.

about 30°N. The horizontal flow of this meridional circulation is so slow that the air spends about a year in the stratosphere, enough time to react the CH_4. Thus practically all CH_4 entering with the air, 0.6×10^{14} g/year, is destroyed.

The other loss of CH_4 to the stratosphere is by upward diffusion driven by the CH_4 gradient in the stratosphere (Fig. 1). The vertical diffusion flux is

$$J = -\rho K_z \frac{\partial M}{\partial z}$$

where ρ is the density, K_z is the vertical eddy-diffusion coefficient, and $\partial M/\partial z$ is the vertical gradient of the CH_4 mixing ratio at the tropopause.

If we take K_Z to be 3×10^3 cm^2/sec in the lower stratosphere and use the gradient from Fig. 1, we obtain a global loss of 0.6×10^{14} g CH_4/year from upward diffusion of CH_4.

Including the stratospheric destruction, the total loss is then 3×10^{15} g/year (Table 3).

TABLE 3

SINKS FOR ATMOSPHERIC CH_4*

Reaction	Destruction rate, g/year
$CH_4 + OH \rightarrow CH_3 + H_2O$ in the troposphere	2.9×10^{15}
Loss to stratosphere in the Hadley circulation	0.6×10^{14}
Loss to stratosphere by vertical eddy diffusion	0.6×10^{14}
Total loss rate	3×10^{15}

*Destruction rates are based on a CH_4 mixing ratio of 1.41 ppM.

ATMOSPHERIC TURNOVER TIME OF CH_4

We can now compare the production and destruction rates of CH_4 by comparing the respective turnover times in Table 4. Considering the large uncertainties in the estimates of production and destruction, the agreement is not too bad. For further comparison, Table 4 also contains an estimate of the turnover time based on the variance of the observed CH_4 concentration in the free atmosphere. Junge has worked out an empirical rule of thumb that relates the turnover time, τ, and the variance expressed as the relative standard deviation of the atmospheric tracer concentration, σ: $\tau\sigma = 0.14$ year. Our measurement of about 400 samples in the free troposphere gave 1.41 ± 0.30 ppM for the average mixing ratio of CH_4. The resulting τ is 0.7 year. Thus the

TABLE 4

TROPOSPHERIC TURNOVER TIME OF CH_4

From biological production alone (Table 2)	2.6 to 8 years
From total production (assuming addition of 20% of dead CH_4)	2 to 6 years
From destruction (Table 3)	1.3 year
From Junge's relation, $\sigma\tau = 0.14$ year	0.7 year

present range of estimates for the atmospheric CH_4 turnover time spans about an order of magnitude from 0.7 to 6 years. The fact that both the destruction rate and Junge's rule give lower turnover times seems to indicate that the source strengths in Table 2 may be underestimated or that some sources are missing altogether.

ATMOSPHERIC PROFILES OF CH_4

Since the CH_4 sources are mainly biologic and bacterial CH_4 production is strongly temperature dependent,[11] we would expect source strengths to vary with season. Consequently, since the turnover time of CH_4 is only a few years, the CH_4 concentration in the atmosphere should also show a seasonal variation. Such a seasonal variation could be used also to determine the tropospheric turnover time of CH_4. With this in mind we obtained a series of vertical profiles of CH_4 in the troposphere up to an altitude of 9 km remote from the local sinks and sources of the earth's surface. Figure 2 shows the seasonally averaged CH_4 profiles obtained over Scottsbluff, Nebr., during 1966 and profiles obtained over

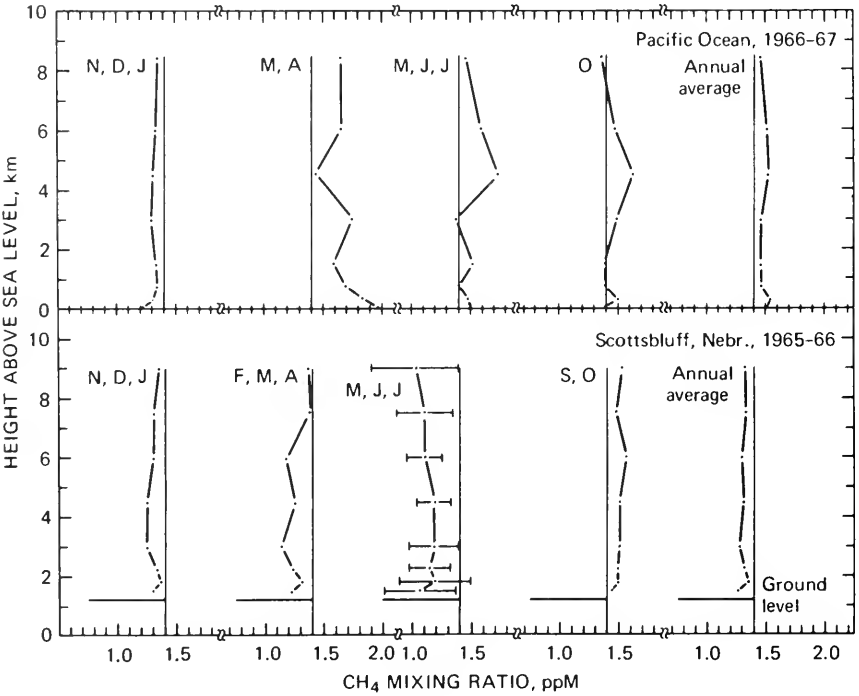

Fig. 2 Seasonally averaged vertical profiles of CH_4 over the eastern Pacific and Scottsbluff, Nebr.[18] The letters show the months over which each profile has been averaged. The vertical lines represent the total average CH_4 volume-mixing ratio in the troposphere: 1.41 ppM. The annual averages are given at the right.

the eastern Pacific about 200 km offshore from Santa Barbara, Calif., during 1966 and 1967 (Ref. 18). Each profile represents an average of two to four individual profiles. If we consider first the Scottsbluff profiles, it appears as if there were a systematic trend in the CH_4 concentration with a maximum in September and October and a decrease during the following months, reaching a minimum in May, June, and July. However, if we look at the standard deviations that are indicated for the summer profile over Scottsbluff, it is obvious that the differences between the seasonal profiles cannot be considered significant at this stage. Further years of observation are required to establish a seasonal variation beyond doubt. In addition, over the Pacific the highest CH_4 concentrations are observed in the spring profiles. The periods during which the fall and winter profiles over Scottsbluff and the Pacific were obtained overlap, and these profiles do show good agreement. The spring and summer profiles were collected in 1966 and 1967, respectively, and the difference between Scottsbluff and Pacific profiles in these cases could include yearly changes in the CH_4 concentration as well as local differences.

The lack of conspicuous seasonal variation in the observed atmospheric CH_4 concentration can have several causes. One is that there are a number of sources, possibly with their seasonal variations out of phase so that only small and short oscillations occur. Another is that the seasonal variation of CH_4 destruction is similar to the seasonal variation of production. In fact, water vapor, ozone, and the total solar-radiation flux that determine the concentration of the OH radical have maximum values in spring or summer. Thus the CH_4 destruction rate should be larger during the warmer seasons, as is the CH_4 production rate. The two seasonal variations tend to cancel each other and leave little imprint on the atmospheric CH_4 concentration.

We were also interested in seeing if the average tropospheric profiles would show systematic gradients, as is the case in the stratosphere. There appears to be at least one. All the Scottsbluff profiles do show a decrease of the CH_4 concentration close to the surface, which seems to indicate that there is a sink of CH_4 close to the surface. Since it is well known that soil microorganisms[19] consume CH_4, the uptake of CH_4 by soil was considered a possible sink. However, preliminary experiments in our laboratory have so far failed to demonstrate that soil microorganisms can utilize the small atmospheric CH_4 concentrations. The annual average profiles do not show significant gradients except those very close to the surface. Because of the higher concentrations in spring, however, the annual average CH_4 concentration over the Pacific is higher than over Scottsbluff.

THE ISOTOPIC COMPOSITION OF CH_4

Another possible source of information is the isotopic composition of CH_4. We have already seen that the ^{14}C content proved quite useful in distinguishing between recent biologic and fossil CH_4 sources. Similarly, the content of the stable isotopes deuterium and ^{13}C in CH_4 may be used to identify the major sources of atmospheric CH_4. This is possible if the isotope content of CH_4 from various sources is sufficiently different. The isotope data now available are summarized in Table 5. The isotope contents are given as δ values in ‰; δ represents the relative deviation of the isotope ratios, deuterium/hydrogen or $^{13}C/^{12}C$, in a sample from that of a standard. For deuterium, the standard generally used is "standard mean ocean water" (SMOW).[20] For ^{13}C, Pee dee belemnite (PDB), a limestone, is used as the standard. A δ value of −100‰ means that the sample contains 100‰ less deuterium or ^{13}C than the standard. From Table 5 it appears that the isotope contents are sufficiently different to distinguish between the various sources, such as marshes, geothermal areas, or natural-gas wells. Unfortunately, however, none of the sources agrees isotopically with the atmospheric CH_4. In particular, the presumably largest sources, paddy fields and marshes, emit CH_4 that has an average ^{13}C content of −65‰, which is much lighter than the average for atmospheric CH_4, −41‰. This difference can be explained by isotopic fractionation in the reaction of CH_4 with OH. Both the collision frequency and the kinetic effects would favor the reaction of the lighter molecule $^{12}CH_4$, so that the CH_4 remaining in the atmosphere is enriched in ^{13}C. This explanation unfortunately also means that the ^{13}C content of atmospheric CH_4 cannot now be used to identify its source and more work on the fractionation during reaction is required. It is interesting to note in this context[21] that the average ^{13}C content of atmospheric CO is about −27‰. If CH_4 is indeed the major source of CO, this would mean that the carbon isotopes must be also fractionated in the oxidation of CO.

Atmospheric CH_4 has a relatively high content of tritium, which is probably due to the release of tritiated CH_4 from nuclear industry. Thus reaction products of CH_4 which contain hydrogen should also have a high tritium content. The molecular H_2 in the atmosphere has a high tritium content anyway because of the release of tritiated H_2 from thermonuclear explosions and nuclear industry. The only other reaction product that is long-lived enough to be collected and analyzed for tritium is formaldehyde, which has been found in rain.[22] Musgrave[23] enriched the formaldehyde from large amounts of rain and indeed observed high tritium contents.[24] This finding lends more support to the above-mentioned reaction scheme.

CONCLUSION

From the preceding descriptions, the following picture of the CH_4 cycle emerges. The atmospheric CH_4 originates at the earth's surface, and about 80% results from the anaerobic decay of recent organic matter. Upon entering the troposphere, it reacts with the hydroxyl radical. This and the subsequent reactions constitute the major sink of CH_4 and a major source of CO. There is

TABLE 5

ISOTOPIC COMPOSITION OF CH_4 FROM VARIOUS SOURCES*

CH_4 source	Deuterium content δ (SMOW), ‰ Mean	Deuterium content δ (SMOW), ‰ Spread	^{13}C content δ (PDB), ‰ Mean	^{13}C content δ (PDB), ‰ Spread	Refs.
Atmospheric	−80		−39.0		39
	−86		−41.2		38
	−94		−43.1		38
			−41.1 ± 2.0	−39 to −43.1	
	−103 ± 23	−76 to −141			28
Marshes and lakes			−65.2 ± 7.4	−52 to −80	29, 30
Glacial drift			−76.3 ± 4.8	−72 to −84	31
Natural gas	−188 ± 17	−150 to −220	−49.6 ± 12.8	−28 to −75	31 to 34
Geothermal	−261.3 ± 27	−225 to −292	−31.6 ± 11.3	−16 to −63	35, 36
Terrestrial plants		−34 to −112†	−25.3 ± 1.6 (−10)	−22 to −30	34, 37
Marine plants	−105 ± 45	−57 to −166	−13.5 ± 2.8	−8.1 to −17	34, 37

*The deuterium and ^{13}C contents in land and marine plants are given in the last two lines for comparison.

†Depends on groundwater: Deuterium in plant material enriched by about 30‰ with respect to average precipitation.

also the possibility that a fraction of the tropospheric CH_4 is taken up by the soil and consumed by microorganisms. A small fraction, about 10%, of the CH_4 enters the stratosphere and is destroyed there, mainly by the same reaction that acts in the troposphere. The resulting reaction products are very important for the chemistry and the water and ozone budget of the stratosphere. The CH_4 cycle is closed at the earth's surface, where the ultimate reaction products of CH_4, CO_2, and H_2O are photosynthesized to plant matter. Some of the plant matter enters the soil as litter, a fraction of which is eventually decomposed anaerobically with the release of CH_4. The CH_4 cycle makes a small but significant contribution to the carbon cycle. Between 1.8×10^{15} and 8.0×10^{15} g CO_2/year pass through it annually. This amounts to a few percent of the annual CO_2 uptake by land plants which is about 130×10^{15} g/year.

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DISCUSSION BY ATTENDEES

Hitchcock: The estimates of the methane productivity of paddy fields by Koyama cannot be trusted. His experiments were conducted in a closed chamber with a nitrogen atmosphere, and he measured the total methane production at the most productive period that would correspond to the period following the flooding of the paddy field. It is questionable whether this rate would continue for the entire year. Furthermore, Koyama equates methane production with injection into the atmosphere. In the natural environment much methane is consumed by methane consumers at the surface of the water or the mud, but this would not occur in his experiments owing to the lack of oxygen.

Ehhalt: Obviously, we need direct measurements of the methane production over swamps.

There is evidence that seems to support the following: it is well known that the tritium content of methane in the atmosphere is unusually high and that the tritium probably comes from the nuclear industry. What this means, of course, is that all the reaction products of that methane should have a high tritium content too. High tritium contents have also been found in formaldehyde, which seems to give some support to the possibility that part of the methane finally ends up in the form of formaldehyde.

ATMOSPHERIC SULFUR AND ITS LINKS TO THE BIOTA

FRANK B. HILL
Department of Applied Science, Brookhaven National Laboratory,
Upton, New York

ABSTRACT

The atmospheric sulfur cycle is reviewed with emphasis on its connections to the biota. Topics discussed concerning these connections are: biometeorological factors affecting rates of uptake of sulfur dioxide by vegetation, the use of regional atmospheric pollution models to predict acidity in precipitation, and factors affecting emission of biogenic sulfur compounds into the atmosphere.

Mankind has long been familiar with manifestations of the existence of compounds of sulfur in the atmosphere and in the biota. These manifestations have often been unpleasant and sometimes threatening. Examples associated with natural phenomena are the foul-smelling emanations from decaying organic matter and acrid fumes spewing forth from volcanoes. Man himself has for a long time taken part in the introduction of this element, and others in association with it, into the atmosphere. In this connection almost four centuries ago the poet Edmund Spenser[1] had occasion to describe a cannon as a "divelish yron Engin," charged "with windy Nitre and quick Sulphur." When it was fired, he said,

> . . .the heavens it doth fill
> With thundring noyse, and all the ayre doth choke,
> That none can breathe, nor see, nor heare at will,
> Through smouldry cloud of duskish stincking smoke. . .

Our modern day "divelish yron Engins," in the form of power plants, smelters, and space-heating devices, are perhaps not so spectacular in the act of emitting compounds of sulfur, and for that matter compounds of nitrogen, into the atmosphere, but their influence is certainly far more widespread and possibly far more inimical to mankind and the world at large.

Today, identification of the phenomena just described with the existence of sulfur compounds in the atmosphere and in the biota goes hand in hand with recognition of the circulations of the element through these reservoirs and of the existence of links between the reservoirs. A continuing study of the circulations and their connections may be of great importance because of the now significant perturbation of the natural circulations resulting from human activity.

In the following discussion the atmospheric circulation and its links to the biota will be surveyed. Interest will be centered on characterizing and understanding this circulation and its inputs and outputs, especially those involving interaction with the biota. Effects on the biota will be mentioned in a limited way.

ATMOSPHERIC SULFUR

The circulation of sulfur through the atmosphere is represented schematically in a highly simplified form in Fig. 1. Also shown are similar representations of the circulation in the biota and of the connections between the two circulations. Starting with the movement through the biota, hydrogen sulfide in soil and water is oxidized to sulfate ion via spontaneous reaction or via the action of colorless and photosynthetic bacteria. Elemental sulfur is produced as an intermediate product in some of these processes. Reduction of sulfate to H_2S occurs via two routes: by assimilatory reduction by plants and microorganisms, followed by nonspecific reduction by a wide variety of bacteria, and by dissimilatory reduction involving anaerobic sulfate-reducing bacteria.

Not all the H_2S produced by these two paths is retained in soil or water. A significant fraction is thought to be emitted into the atmosphere. Once in the atmosphere, H_2S is oxidized to SO_2 and ultimately to a sulfate compound. Among the processes by which SO_2 and sulfates are removed from the atmosphere are two which involve important interactions with the biota: (1) the absorption of SO_2 by vegetation and soils and (2) the deposition of sulfur in precipitation, largely as sulfates, on soils and in water bodies in which plant and animal life exists. These two processes of removal from the atmosphere and the process of emission of biogenic H_2S are the links between the two reservoirs which we will consider in some detail later on.

Origin and Fate of Atmospheric Sulfur Compounds

A more complete but still brief description will now be given of this topic, based on the recent reviews of Robinson and Robbins[2] and Kellogg et al.[3] Sulfur occurs in the atmosphere principally in the three forms already mentioned: H_2S, SO_2, and sulfates. Included as sulfates are sulfuric acid, metallic sulfates, and ammonium sulfate.

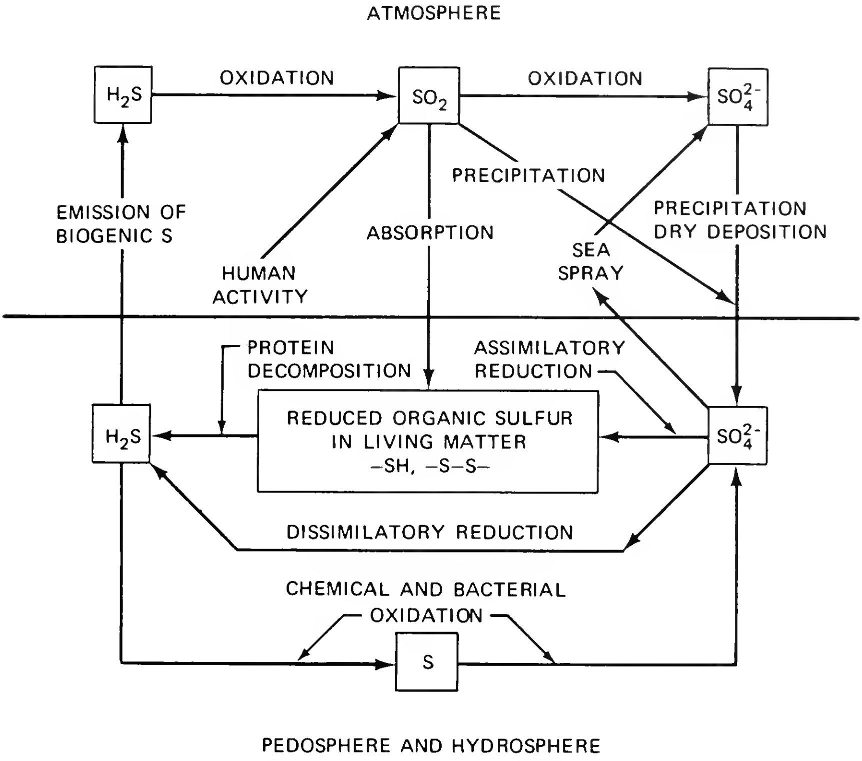

Fig. 1 The circulations of sulfur through the atmosphere and the biota.

Hydrogen sulfide, containing sulfur in its most reduced form, originates, as indicated earlier, from the nonspecific reduction of organic sulfur and from sulfate reduction by anaerobic bacteria. These are thought to be the principal processes by which H_2S is generated on a global scale. In relatively small amounts H_2S is derived from industrial processes, such as petroleum refining and kraft pulp manufacture, and from volcanoes. In the atmosphere, H_2S may undergo oxidation by atomic oxygen and ozone to yield SO_2 and ultimately sulfate. In a rural atmosphere the concentration of H_2S has been found[4] to be of the order of 0.3 $\mu g/m^3$, but the method used has been challenged, and actual background concentrations are presumed to be significantly lower than this value. (See the section on Emission of Biogenic Hydrogen Sulfide.) The residence time of H_2S in the atmosphere is estimated not to exceed 1 day and is probably considerably less than 1 day.

Sulfur dioxide is produced in the atmosphere as a product of H_2S oxidation. It is emitted into the atmosphere in large quantities as a product of fossil-fuel combustion and of ore smelting and in lesser quantities from volcanic action. Coal burning is the major source of SO_2 from fossil fuels. Within the atmosphere, SO_2 is thought to be oxidized to sulfate via a number of mechanisms, including photochemical reactions in air and catalytic reactions on particles or in solution in water droplets. Although much careful laboratory study has been given to these reactions, considerable uncertainty remains concerning the relative importance of the different reactions in the atmosphere. In addition to disappearance via chemical transformation within the atmosphere, SO_2 may be removed by absorption at the atmosphere–earth interface. Sites for absorption include the surfaces of soil, vegetation, and water bodies. Measurements of the concentration of SO_2 in air at sites remote from industrialized or urban areas have yielded values in the range <1 to $5\ \mu g/m^3$. Concentrations as high as several thousand $\mu g/m^3$ have been reported in heavily industrialized areas. The residence time of SO_2 in the atmosphere is highly dependent on the presence of other pollutants and hence may be a function of locale. In urban areas it may be measured in hours, whereas in rural regions it may range up to a week.

Sulfates in the atmosphere are injected there as sea-salt particles from sea spray or they are produced in the atmosphere as the product of the oxidation of SO_2 and, earlier, H_2S. Particles generated from sea spray are generally thought to be somewhat larger in size than those of anthropogenic or biogenic origin. As such they are more readily subject to removal near their point of origin by precipitation scavenging and dry deposition. Sea-spray sulfate is thus involved in a cycle over the oceans which is almost closed. Ninety percent of it returns to the oceans, and 10% is carried over land.[5] Sulfate particles of anthropogenic or biogenic origin are smaller in size than particles of marine origin and are subject to transport over longer distances before removal by precipitation scavenging and dry deposition. The amount of such sulfate, called excess sulfate, is calculated by subtracting the sea-salt sulfate present from the total. Sea-salt sulfate is calculated as the product of the chloride content of the aerosol and the sulfate-to-chloride ratio in seawater. The tropospheric sulfate aerosol is found in concentrations in the range 0.5 to $5\ \mu g/m^3$ in regions remote from industrial emissions. The residence time of the aerosol is estimated to be of the order of several days to 1 week.

Removal of sulfur from the atmosphere by precipitation scavenging occurs via two processes: rainout and washout. Rainout refers to in-cloud removal by such mechanisms as condensation of droplets on sulfate particles or absorption of SO_2 by cloud droplets with subsequent oxidation to sulfate. Washout refers to removal by precipitation as it falls below clouds. According to a theoretical study by Beilke and Georgii,[6] in polluted atmospheres where below-cloud SO_2 concentrations are high, washout of SO_2 can contribute the major portion of the sulfate found in precipitation, whereas in rural unpolluted atmospheres rainout of sulfate particles can be dominant.

An important point to note in connection with removal of sulfur from the atmosphere in precipitation is that such precipitation may be acid in nature. Hydrogen ions are produced when SO_2 is dissolved in water and when it is oxidized to sulfate. The extent to which these hydrogen ions persist depends on the extent to which basic substances are present in the water droplet. In any case, acidity present to some degree in precipitation in association with sulfate ion may be expected and is often found.

The Global Atmospheric Sulfur Budget

Global budgets have recently been prepared by a number of writers.[2,3,5,7,8] The principal sources and sinks and their transfer rates as derived by Kellogg and coworkers[3] are given in Table 1. Transfer rates in Table 1 and elsewhere in the paper are given in units of millions of metric tons of sulfur per year. Details of the derivation of the transfer rates in this and other tabulations will not be given here but may be found in the original papers. The following comments, however, are of present interest.

The anthropogenic mobilization of sulfur represented by fertilizer application amounts to 26 million tons/year according to recent estimates.[8] Estimates of emission into the atmosphere resulting from human activity range from 50 to 70 million tons/year. Thus the contribution to the atmosphere represents the major fraction of human mobilization.

Over 90% of man-made emissions come from the northern hemisphere, and thus the distribution of these emissions is highly nonuniform. Man-made emissions doubled in the period from 1940 to 1965. It is projected that the present rate will more than double by the year 2000.

TABLE 1

GLOBAL ATMOSPHERIC SULFUR BUDGET[3]

	Transfer rate, 10^6 tons S/year		
	Terrestrial	Marine	Total
Sources			
Human activity	50		50
Biogenic H_2S	90		90
Sea-spray sulfate		43	43
Total			183
Sinks			
Precipitation and dry deposition	96	72	168
Absorption of SO_2 by vegetation and soils	15		15
Absorption of SO_2 by oceans		?	
Total			183

No data are available on which to base estimates of biogenic emissions. Instead, transfer rates for this source are determined by difference. Thus, assuming that the sulfur burden of the atmosphere is not changing on the time scale of 1 year, the biogenic emission rate is set equal to the source deficit usually found. More discussion of this point will be given below in the section on biogenic emission.

Anthropogenic and biogenic emissions represent the major net emissions since sea-spray sulfate largely returns to the oceans.

Precipitation scavenging and dry deposition are by far the largest removal processes. Precipitation scavenging is estimated to account for 80% of the sulfate removal processes. Removal of SO_2 by soils and vegetation accounts for about 14% of the sulfur-removal processes over land according to Kellogg et al. These same authors find insufficient evidence to decide whether the oceans are a sink for SO_2 or a source of that compound.

Global models for the atmospheric sulfur budget have so far avoided the necessity of making estimates of the rates of chemical transformations within the atmosphere by dealing only with the inputs and outputs of the element regardless of chemical form. When and if such rates can be adequately characterized, then separate budgets can be prepared for H_2S, SO_2, and sulfates, and the resulting models may be more useful for predictive purposes. Without making this differentiation, global budgets are perhaps most useful in pointing out areas in which further investigation is required.

A further limitation on the usefulness of global sulfur models is the large spatial variation in source distribution in combination with atmospheric residence times that are short compared to global atmospheric mixing times. These factors tend to make regional and even local models of more practical interest.

ABSORPTION OF SULFUR DIOXIDE BY VEGETATION AND SOILS

We now turn to a more detailed consideration of the links between the atmosphere and the biota, and we discuss first the absorption of SO_2 by vegetation and soils. The point to be made here concerns the basis for estimating global removal rates and the need for more data describing uptake by these processes.

The rate of removal of SO_2 by vegetation or soils may be expressed as a concentration driving force divided by an overall resistance. If the sink is regarded as perfect, i.e., if the concentration at the surface is zero, then the concentration in the bulk air becomes the driving force, and the reciprocal of the overall resistance is called the deposition velocity, the effective velocity at which a molecule of SO_2 approaches the absorption site. In the case of vegetation, the deposition velocity is the reciprocal of the sum of the resistances due to the lower atmosphere, the vegetation canopy, the boundary layer adjacent to the leaf surface, the stomatal opening into the interior of the leaf, and the water-film lining of the walls of the cells in the mesophyll. For soils the deposition velocity reflects the atmospheric resistances plus the resistance for absorption into a water film on the surface or for adsorption onto a solid surface. The atmospheric resistances are dependent on such variables as wind velocity and atmospheric stability, whereas the interior leaf resistances vary with degree of stomatal opening and hence with factors that affect stomatal opening, such as light intensity, humidity, soil moisture, and temperature. Many other factors are probably also important in determining leaf resistance. Canopy resistance is a function of wind velocity and canopy structure.

To date, estimates of the global rate of SO_2 removal by vegetation have been based on the implicit assumption that the major resistance to mass transfer is in the atmosphere[3] or that the effective deposition velocity is that corresponding to uptake rates of shallow vegetation canopies in daylight.[2]

Experimental studies on uptake by vegetation are scarce, but the available data suggest that, in the preparation of global estimates, biometeorological factors should be given more emphasis. The principal results of three pertinent investigations are summarized in Table 2 and discussed in the following paragraphs.

Katz and Ledingham,[9] cited by Robinson and Robbins,[2] placed fumigation chambers over alfalfa in the field and measured the decrease in SO_2 concentration in mixtures of $2300\ \mu g\ SO_2/m^3$ of air passed through the chambers. Maximum uptake by the plants and soil corresponded to a deposition velocity of 1.3 cm/sec. At night the absorption rate dropped to about 10% of the maximum, and for shaded plants the rate was 20% of the maximum.

Spedding[10] has measured SO_2 uptake by barley leaves at concentration levels found in rural air (10 to $20\ \mu g/m^3$) and in urban air (100 to $150\ \mu g/m^3$). Barley plants at the three-leaf stage were exposed to a continuous flow of ^{35}S-tagged SO_2 in air with a linear velocity of 2 cm/sec, and the rate of uptake

TABLE 2

SULFUR DIOXIDE UPTAKE BY VEGETATION

		Overall conductance, cm/sec			
Plant	**Exposure**	**Leaf, stomates open**	**Leaf, stomates closed**	**Canopy, stomates open**	**Refs.**
Alfalfa	Field			1.3	9
Barley	Chamber	0.2	$\leqslant 0.03$	1.5 (est.)	10
Alfalfa	Chamber			2.5	11
Alfalfa	Field			2.0	11

was determined by measurement of the ^{35}S activity in the leaves. Degree of stomatal opening was determined with a pressure porometer.

Uptake rates varied markedly with condition of stomata. Rates with open stomates were at least six times greater than those with closed stomates. The stomates were open at humidities higher than about 80%. Below this level there still was a variation with humidity, and this variation was taken to reflect absorption of SO_2 by a film of water on the leaf surfaces. Although the external (fluid dynamic) resistance was appreciable even with open stomata, the major resistance was always the internal leaf resistance. The average uptake rate with open stomates corresponds to a deposition velocity of 0.2 cm/sec. If the leaf surface area per unit area of ground is taken into account, then the deposition velocity for a canopy of barley becomes 1.5 cm/sec.

Hill[11] has made measurements of the uptake of several pollutants by alfalfa and oat canopies in a chamber with a floor area of 1.4 m^2. Measurements of effects of wind speed, light intensity, canopy height, and pollutant concentration were made. For SO_2 the uptake rates in alfalfa, at a light intensity corresponding to approximately half of midday sunlight, varied linearly with concentration over the range 140 to 700 $\mu g/m^3$, corresponding to a deposition velocity of 2.5 cm/sec. In a field experiment with the same plants, carried out at the National Reactor Testing Station in Idaho using ^{35}S-tagged SO_2, deposition velocities found were 20% lower, representing encouragingly close agreement between chamber and field experiments.

On the basis of the evidence just cited, nighttime uptake of SO_2 by vegetation might be expected to be much reduced from daytime uptake. However, Martin and Barber[12] have reported data which suggest that other phenomena may be responsible for maintaining high rates at night. These authors were interested in monitoring the concentration of SO_2 in the vicinity of a power plant. The sampler intake probe was inadvertently located near a hedge that evidently was a sufficiently effective sink for SO_2 to give significantly lower SO_2 readings than would have been otherwise expected. The hedge was found to be an effective sink at night as well as in the daytime, and the nighttime losses were greater at higher relative humidities, suggesting that uptake by dew was important.

Data on rates of SO_2 uptake by soils are even scantier than those for uptake by vegetation. Laboratory measurements have been made on uptake by soil samples,[13] but these are not readily related to field conditions. Measurements exist for building materials, including limestone,[14] and Liss[15] has made estimates of specific uptake rates in natural water bodies. For the range of pH values from 4 to 9, normally encountered in the environment, Liss found the major resistance to SO_2 uptake to be in the gas phase. He showed this to be true whether the air and water were quiescent or in turbulent motion. Presumably this would be true for uptake in films of moisture on soils. Thus, to the extent that soil uptake involves absorption in water films, knowledge of the atmospheric resistance may be adequate for the estimation of soil uptake rate.

The foregoing discussion suggests that biometeorological factors should be given further consideration in making estimates of vegetation uptake rates but that much more information is needed before meaningful refinement of present estimates can be undertaken. The following are but a few of the factors that need study: diurnal and seasonal variation, effect of shading, kind of vegetation, growth stage, variation within and between species and within individual plants, canopy uptake compared with uptake by individual leaves, and stresses of various kinds.

Refinement of present global estimates may not have a major effect on the overall atmospheric budget, although such refinement is desirable in principle. The information that would result from further research on uptake by vegetation would be perhaps more practically useful in connection with evaluation of regional and local budgets and in understanding the relation of uptake to injury. Injury has so far not been noted at background concentrations but has been found in susceptible plants at concentrations well below those presently found in urban atmospheres.

SULFATE REMOVAL BY PRECIPITATION SCAVENGING

As mentioned earlier, almost all the sulfur in the atmosphere is believed to return to the earth's surface via precipitation scavenging and dry deposition of sulfates, with precipitation scavenging accounting for about 80% of the total of the two processes. Also, the material removed in precipitation is often acid in nature. This latter feature represents the point of interest in this discussion.

Over the past few decades, acidity in association with high sulfate concentrations has been noted in soils and groundwaters in many places in the United Kingdom and in the United States and Canada.[16] In many instances the locales in which the acidity was found were in the immediate vicinity of smelters or other types of large emitters of SO_2. Likewise, acidity in precipitation has been noted during the same time period in close proximity to many industrial centers in various parts of the world.[17,18] In these cases the transit time from the locale of SO_2 emission to the locale of detection of acidity in soil, groundwater, or precipitation was short compared to the lifetime of SO_2 in the atmosphere.

During the past 15 years, evidence has been accumulating to show that acidity in precipitation has become significant at relatively great distances from, but still downwind of, major industrial centers. The transit time to such distances, which range up to 1000 km or more, is of the order of a day to a few days, which is comparable to the lifetime of SO_2 in the atmosphere. During the 15-year period, the acidity has steadily increased, roughly in parallel with industrial growth. This evidence has been well documented by Engström[19] for parts of Sweden and Norway.

Data reported in Engström's study for the year 1965 show that the excess acid* in precipitation in Scandinavia closely paralleled deposition of excess sulfate in precipitation (Fig. 2), and during the past 15 years intrusion of excess acidity into southern Scandinavia from a southwesterly direction has been increasing (Fig. 3). The pH of rainwater[20] during this time period was found to be as low as 2.8. Acidity in rainfall may be at least in part responsible for the fact that many lakes and rivers in Sweden are increasing in acidity (Fig. 4).

Acid groundwater may lead to leaching of nutrients required for growth of agricultural and forest vegetation, leading to reduced productivity. Microbial life may also be affected. If present trends continue, the pH of lakes in Sweden evidently will within a foreseeable time reach a level critical for the life of fishes.

Of great interest is the question of the origin of the acidity in precipitation found in Scandinavia. Several kinds of circumstantial evidence point to man-made emissions of SO_2 in northern and western Europe. First, as stated by Engström, the estimated deposition of anthropogenic sulfur in precipitation within Sweden exceeds the anthropogenic emission from Sweden. This is also the case for Norway, but the opposite is found in Denmark, Holland, West Germany. France, and the United Kingdom. Second, also in Engström's report, an air-parcel trajectory analysis is described in which the end points of a large number of 24- and 60-hr trajectories were determined for parcels originating from a single point in north central Europe. It was found that the end points were fairly symmetrically distributed around the point of origin but with a drift of the center of gravity to the east and northeast. Third, Reiquam[21,22] has applied an air-pollution simulation model to the region. The model was developed to treat regional air-pollution episodes in which relatively stagnant air masses develop and persist over a large area for several days. The region is considered to be laid out on a square grid with a grid spacing in the case of the calculation of interest of 2° of latitude and longitude. Over each square a box was visualized, which for the calculation of interest was 3 km high, corresponding to the assumed mixing depth of the atmosphere. The air within each box was assumed to be well mixed. Sulfur emissions were tabulated for each box on the basis of fuel-consumption data for the region and an assumed sulfur emission of 2.5% of the fuel burned. Simple mass balances were devised which used the emission data and mean values of local wind velocity to compute the movement of pollutant sulfur from box to box. The distribution of total sulfur concentration in the air over northern and western Europe as calculated at the end of a simulated 10-day wintertime episode of light southwesterly wind is shown in Fig. 5(a). The effects of cessation of operation of sources in the United Kingdom and in northern Europe are shown in Figs. 5(b) and 5(c). Reiquam noted that his model did not take into account chemical transformation in the atmosphere, processes of removal at the earth–air interface, especially precipita-

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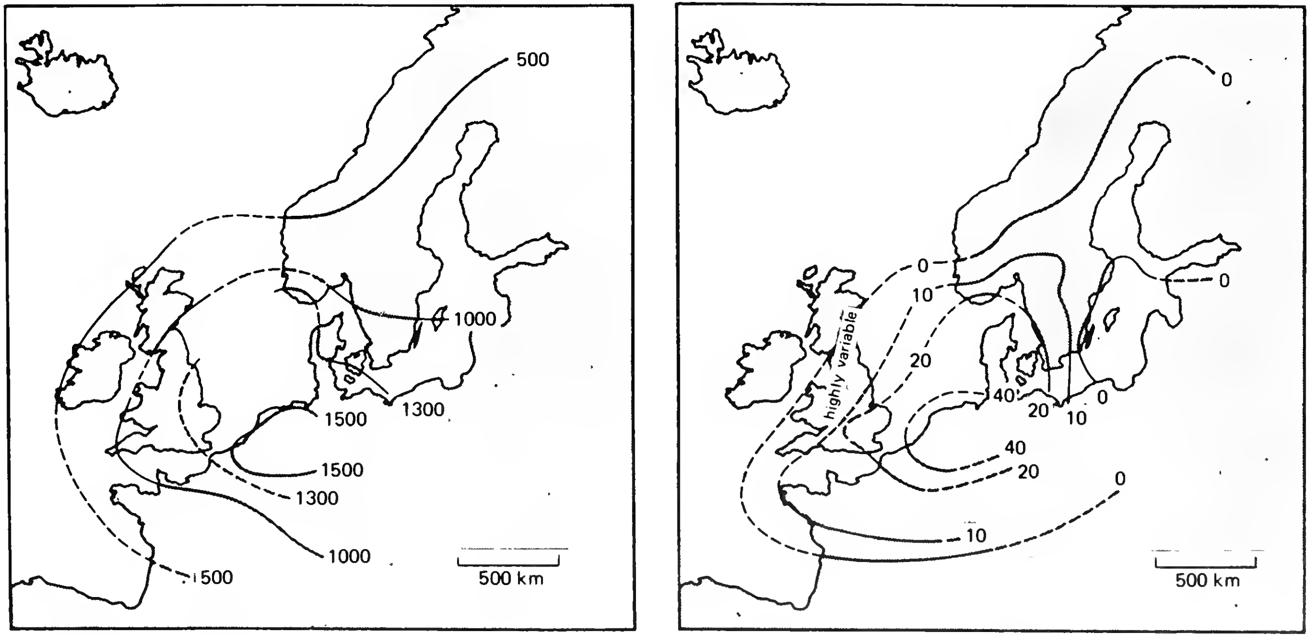
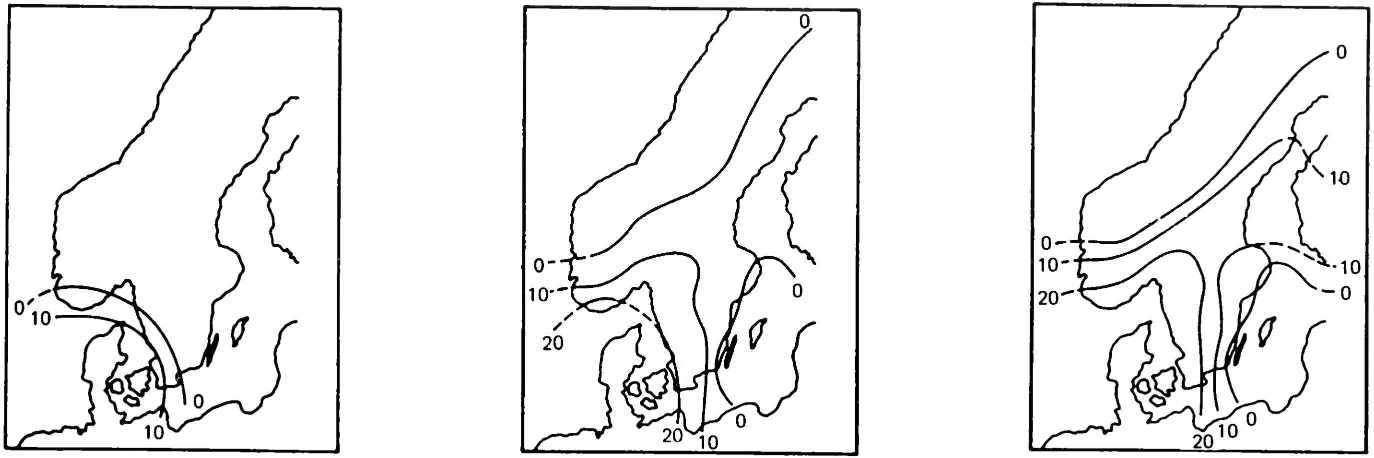
*The term "excess acid" is defined as the total acidity in precipitation over the time period of 1 year minus the total amount of base.



(a)

(b)

Fig. 2 (a) Deposition of excess sulfur in mg S/m^2, and (b) deposition of excess acidity in mg H^+/m^2, in northern Europe for the year 1965. From Engström.[19]



1955

(a)

1965

(b)

1970

(c)

Fig. 3 Deposition of excess acid in mg $H^+ m^{-2} year^{-1}$ for the years shown. From Engström.[19]

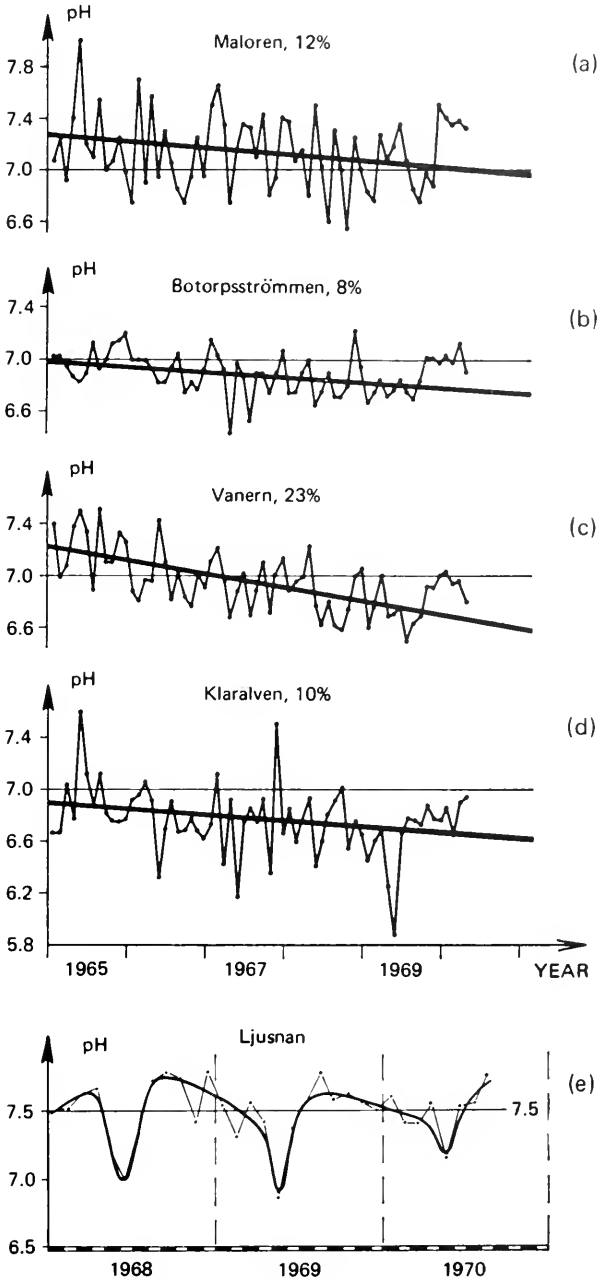
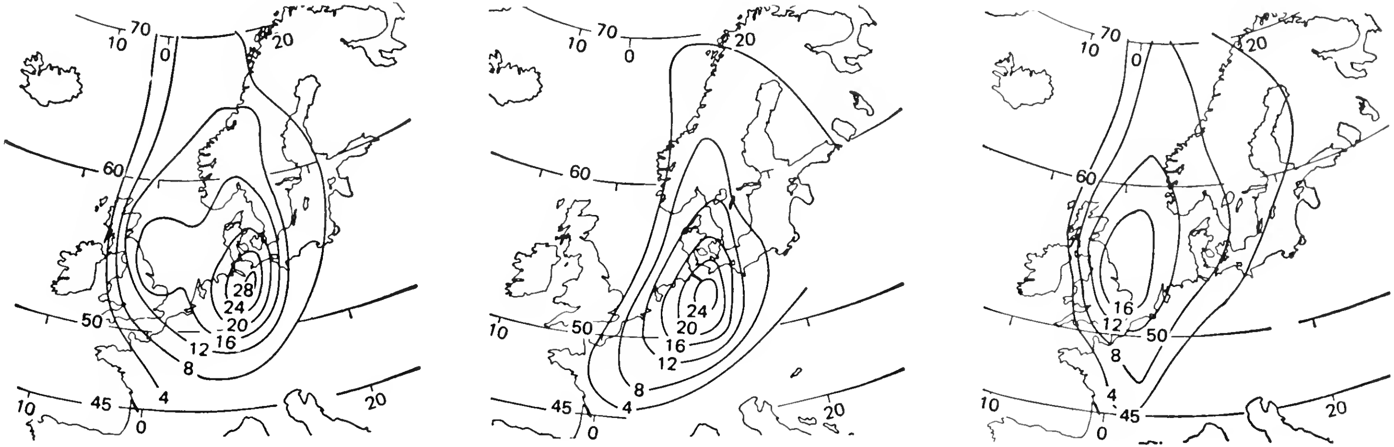


Fig. 4 The pH changes in rivers and lakes in Sweden. The four upper curves are for rivers and lake outlets in southern Sweden. The fifth curve is for the Ljusnan River in central Sweden and shows the effect of washout of acid water every year following spring melting. From Engström.[19]



(a) (b) (c)

Fig. 5 Reiquam's[22] calculated mean concentration of total sulfur, μg/m^3, during a simulated air-pollution episode in winter: (a) sulfur emitted in all western European countries; (b) no sulfur emissions in the United Kingdom; (c) no sulfur emissions in Germany, Belgium, Netherlands, and Luxembourg. [From Howard Reiquam, Sulfur: Simulated Long-Range Transport in the Atmosphere, *Science*, 170: 319 (1970).]

tion scavenging, and natural emission of sulfur compounds. All these processes would have to be incorporated into any model attempting to relate observed acidity in precipitation to remote sources since on a regional or continental scale these processes would be likely to be of importance.[23] Information on the alkalinity of aerosols in the region would also be required.

There will no doubt be much further interest in regional or continental air-pollution models and in other means of relating sources and remote receptor regions as more evidence accumulates showing their need. In this regard, Pearson and Fisher[24] and Likens, Bormann, and Johnson[18] have recently reported findings of acidity in precipitation in the northeastern United States. The findings are similar to those described by Engström for Scandinavia, and there is also some evidence of increases in acidity in precipitation in the region with time. Likens and coworkers note that, in addition to anthropogenic sulfur compounds, anthropogenic nitrogen compounds may be involved in the production of acid precipitation.

Schmidt and Velds[25] have added a note of caution in connection with the process of associating changing pollutant concentrations with changes in anthropogenic emission rates. They showed that falling concentrations of SO_2 in the vicinity of Rotterdam over the course of a few years could better be ascribed to short-term meteorological variations than to the known decreasing emission rate in the area. The successful assessment of man's role in setting off the chain of events leading to high levels of excess acidity in precipitation on a regional or continental scale will require much further work defining the processes involved. In view of the possible ecological consequences discussed by Engström and Likens et al. and in view of the fact that relations between nations are involved, the effort should be more than justified.

EMISSION OF BIOGENIC HYDROGEN SULFIDE

This is the least well-known component of the atmospheric sulfur budget. In fact, there appears to be no direct experimental evidence that may be used to estimate the magnitude of this emission. It is then not surprising that estimates of the magnitude of the emission in five studies of the sulfur cycle made during the past decade range over almost a factor of 3. Putting this estimate on a sound footing is crucial to the understanding of the sulfur cycle and the importance of man's role in that cycle. This is so since anthropogenic and biogenic sources are evidently the only major net sources. If, for instance, the actual amount of H_2S emitted is considerably less than the least estimate to date, then emission from man-made sources becomes virtually the single driving force for the global sulfur cycle.

A second reason exists that provides strong motivation for obtaining data on H_2S emission rates. Until recently, H_2S was the only sulfur compound mentioned in the literature on the sulfur cycle as a volatile component in the circulation of sulfur through the biosphere, and this compound was therefore the one put forth whose emission would make up for apparent emission deficits. It was and is a convenient choice since its fate is thought to be known and to be consistent with other notions about the sulfur cycle, i.e., it is thought to be oxidized to SO_2 and sulfates, the other principal forms of sulfur in the atmosphere.

However, in possible contradiction of this view, evidence has recently been obtained which offers the possibility that other volatile compounds of sulfur of biogenic origin, such as dimethyl sulfide, may serve in place of H_2S in contributing to the apparent source deficit. If these other compounds should in fact be found to constitute the principal biogenic contributions to the atmosphere and if, in addition, they are not converted in the atmosphere largely to SO_2 and sulfate, then it will not be possible to account for the large amounts of these latter materials which are removed from the atmosphere, and present concepts of the sulfur cycle will be called into question.

In the following discussion we will, at least at the outset, continue to regard H_2S as the principal compound of biogenic origin emitted into the atmosphere. Toward the end of the section, we will present the evidence for emission of other biogenic sulfur compounds.

In recently prepared estimates of the atmospheric sulfur budget, a number of different approaches were used to arrive at the biogenic H_2S transfer rate. Junge[7] derived a terrestrial emission rate of 70 million tons S/year by assuming that the sulfur absorbed from the atmosphere by soil and vegetation was released to the atmosphere as H_2S. By requiring the inputs and outputs of the pedosphere to be in balance, Eriksson[5] estimated a terrestrial emission of 110 million tons/year. On a similar basis, Robinson and Robbins[2] estimated 68 million tons/year, and Friend[8] estimated 58 million tons/year.

Estimates of emission from the oceans range from 170 (Ref. 5) to 30 million tons/year (Ref. 2). These figures follow from invoking a balance of total sulfur in the atmosphere over the oceans or within the oceans themselves. Kellogg et al.[3] assert that the oceans cannot be a source of H_2S, since its oxidation within seawater would be too rapid to permit appreciable escape to the atmosphere. Instead, they suggest that emissions must be terrestrial in origin and that shoreline emission may be important. In separately balancing total sulfur inputs and outputs in the northern and southern hemispheres, they estimate a total global emission of 90 million tons/year.

The overall emission process to be characterized has the following features. As mentioned earlier, hydrogen sulfide is generated by bacteria in two ways. In one way, dissimilatory sulfate-reducing bacteria mediate the reduction of sulfate ion to H_2S, obtaining the necessary reducing power from organic material.[26] The organisms involved are strictly anaerobic and may be found in water and sediments and in terrestrial soils. In the second way, the source of sulfur is the reduced organic form found in dead plant and animal matter. Sulfur in living cells is predominantly in the form of protein sulfur. The release of sulfide from proteins is a widespread property among bacteria.[27] Organisms that perform this function may be found in both aerobic and anaerobic environments, especially those containing large amounts of readily decomposable organic matter. In aerobic environments, protein sulfur is usually released as sulfate but sometimes as H_2S. In anaerobic environments, sulfide is the released form.

Regardless of type of bacterial mediation, the locale of generation is probably in an aqueous medium, whether in a film of moisture in soil or within the sediments or bulk water of lakes or oceans. The chemical form of the generated compound will vary with pH.[28] Ionization constants for H_2S in solution at 18°C are

$$k_1 = \frac{[H_3O^+][SH^-]}{[H_2S]} = 0.9 \times 10^{-7}$$

$$k_2 = \frac{[H_3O^+][S^{2-}]}{[SH^-]} \simeq 10^{-15}$$

From these expressions it can be seen that undissociated H_2S will be the more abundant form in acid waters, whereas SH^- will predominate in basic waters. Dissociation to sulfide ion will always be very small. We will henceforth refer to the three species H_2S, SH^-, and S^{2-}, collectively, as sulfide except when it is necessary to make a distinction among them.

The sulfide generated as indicated above may be transformed chemically or biologically to other forms, or it may be transported to the air–water interface and there be released to the atmosphere as H_2S. Some of the features of these processes are described in the following paragraphs.

One of the possible chemical transformations involves precipitation as a metallic sulfide.[29] The presence of ferrous iron or other heavy metals in solution may thus limit the total sulfide concentration in solution by precipitate formation. The limitation will be a function of pH. Very small amounts of total sulfide will coexist with ferrous iron in solution in neutral or basic waters, whereas appreciable quantities may coexist in acid waters. Sulfide generated in excess of that required to remove metal as insoluble sulfides will remain in solution in basic waters.

In a second possible transformation, the sulfide will be subject to oxidation by dissolved oxygen. Rates of this reaction have been studied in laboratory and field experiments by Skopintsev, Karpov, and Vershinina,[30] Östlund and Alexander,[31] and Cline and Richards.[32] Apparent rate constants are available, but reaction details are not well known. Reaction products include thiosulfate, sulfite, and sulfate. Östlund and Alexander show that in seawater containing 5 ml O_2 per liter the mean lifetime of H_2S is of the order of 20 min.

Several kinds of bacteria are capable of oxidizing sulfide. Chemolithotropic sulfur bacteria are capable of utilizing reducing power obtained from the oxidation of reduced sulfur compounds in order to reduce CO_2 to form cellular organic matter. Some heterotrophic bacteria are also capable of oxidizing reduced sulfur compounds, apparently without utilizing the resultant energy. Certain photosynthetic bacteria can use H_2S and other sulfide compounds as electron donors.

The relative importance of biological and nonbiological oxidation of sulfur compounds in sulfur deposits[33] and in lakes[34,35] has been investigated using ^{35}S-labeled sulfide. Depending on oxygen availability, bacteria may play an important although perhaps secondary role in the oxidation of H_2S.

Transport of sulfide to the water surface may occur by a number of mechanisms including molecular and turbulent diffusion. In the absence of chemical or biological oxidation, the average distance through which a sulfide ion or molecule with a diffusion coefficient D will diffuse during a time t is $(2Dt)^{1/2}$. Then during the 20-min lifetime of H_2S in oxygen-bearing seawater found by Östlund and Alexander,[31] the sulfide could traverse distances of the order of 1 mm by molecular diffusion ($D \simeq 10^{-5}$ cm^2/sec) and 1 m by turbulent diffusion [$D \simeq 10$ cm^2/sec (Ref. 36)]. As a first approximation, in the presence of dissolved oxygen and sulfide-oxidizing bacteria, escape of H_2S is then conceivable from layers of stagnant water less than about 1 mm in depth and from turbulent water bodies up to about 1 m in depth. H_2S can conceivably also be brought to the surface of water bodies by convective flow or in gas bubbles.

The rates of movement of H_2S out of the water will be a function of pH. At low pH most of the sulfide will be present as undissociated H_2S, resulting in a high effective concentration driving force for transport. In basic waters the opposite will be true.

Rates of oxidation of H_2S in the atmosphere are not well known. Laboratory measurements exist for reactions with atomic oxygen[37] and ozone.[38,39] Most authorities suggest, on the basis of these measurements, that the oxidation of H_2S in the atmosphere is rapid, probably resulting in a half-life considerably less than 1 day.[2,3] After emission into the atmosphere, H_2S may also be subject to removal from the atmosphere by absorption on terrestrial and marine surfaces.

From the foregoing description of the phenomena leading to H_2S emission, various writers have drawn some of the following conclusions regarding expected locales of emission. Both land and marine sources of biogenic H_2S have been envisioned. On land H_2S may be emitted from swamps and bogs, from lakes, and from soils when wet and therefore in soils with a high water table. Johansson,[40] cited by Eriksson,[5] has obtained some data that provide indirect evidence for the emission of H_2S from the soil of potted plants. Marine sources may include marshes, intertidal flats, and polluted harbors.

The suggestion that H_2S may not be the missing link in the atmospheric sulfur budget has recently come from Lovelock, Maggs, and Rasmussen.[41] In laboratory experiments these authors have found dimethyl sulfide in seawater and have found its concentration to be of the order of 4×10^{-12} g/ml. Also, they have measured its rate of emission from marine algae, living and dead tree leaves, and terrestrial soils. Average emission rates from algae were of the order of 70 picaliters g^{-1} hr^{-1} and from leaves and soils, 60×10^{-12} g g^{-1} hr^{-1}. The standard deviations for all these measurements were large. So far Lovelock et al. have been unable to detect dimethyl sulfide in the atmosphere, although they state that failure to do so may have been due to oxidation occurring between collection and analysis of samples.

As noted by Lovelock et al. in Ref. 41, Bentley et al.[42] have found the spectrum of the products of the simulated atmospheric photooxidation of dimethyl sulfide to include dimethyl sulfoxide, methane sulfonic acid, sulfur dioxide, and sulfuric acid. Lovelock et al. suggest that, since dimethyl sulfoxide may be one of the first products appearing in the oxidation reaction, its low volatility and hygroscopic nature may cause it to be readily removed from the atmosphere before further oxidation. If so, then dimethyl sulfide would be less a source of sulfate aerosol than are the inorganic sulfur compounds, H_2S and SO_2.

It should be noted that a number of plant families are known to have methylated sulfur compounds as constituents.[43] Also, Starkey[44] and his students have shown that, in the dissimilation of methionine brought about by certain bacteria or bacteria and fungi, the volatile sulfur compounds methyl mercaptan and dimethyl disulfide appear as products.

Up to now the characterization of the biogenic sulfur-compound emission process has been in part held back by the lack of sufficiently sensitive analytical methods for the measurement of the concentrations of H_2S, and now of other compounds such as dimethyl sulfide, in the atmosphere. For H_2S, background concentrations have been assumed to be of the order of 0.3 $\mu g/m^3$ or less, whereas available analytical methods could not measure concentrations less than about 1.5 $\mu g/m^3$. Recently a method has been devised which is reported[45] to permit measurement of concentrations as small as 0.002 $\mu g/m^3$. This method involves collecting the H_2S on $AgNO_3$-treated filter paper, recovering the resulting Ag_2S from the filter paper with alkaline cyanide solution and analyzing for the released sulfide ion fluorometrically. When this method was used in unpolluted air in Colorado, concentrations in the range of 0.03 to 0.1 $\mu g/m^3$ were found. For dimethyl sulfide and, presumably, other related sulfur compounds, sensitive gas chromatographic methods of analysis evidently are available[41] and will soon be described in the literature.

In view of the analytical developments just described, studies of the emission of biogenic sulfur compounds now appear feasible. Such studies might involve the measurement of vertical fluxes of these compounds into the atmosphere along with the establishment of profiles of physical, chemical, and microbiological properties of the locale of generation and emission.

In certain coastal regions, emissions of what is presumed to be biogenic H_2S are so strong as to blacken paint and tarnish silver in nearby homes. Emission rates and other features of the overall emission process which apply to these areas should be readily observable.

CONCLUSION

In this paper brief reviews have been given of the atmospheric sulfur budget and of the links through which sulfur in the atmosphere exerts effects on the biota or is itself affected by the biota. Certain research needs aimed at obtaining a better understanding and characterization of these links were cited in the course of presenting these reviews.

One of the points of greatest interest concerns assessment of man's role in affecting these interactions. The emission rate for anthropogenic sulfur is one measure of that role. Even though this emission rate is one of the better known transfer rates in any atmospheric budget—whether local, regional, continental, or global—its importance is, in general, difficult to assess because of the lack of knowledge on the same scale of accuracy of transfer rates for natural processes, especially those for biogenic emission. However, in the case of sulfate removal by precipitation, it does appear that man's activities may be increasingly affecting the biota on a geographically large scale.

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DISCUSSION BY ATTENDEES

Reiners: Data from two unpublished studies on the effects of acid rain on soils may be of interest. Drs. Dominski and Bormann of Yale University, and Dr. Reynolds of Dartmouth College have treated New Hampshire soils with solutions of increasing SO_4^{2-}—acidity. In general, leaching produced little metallic cation release until pH was reduced to 3.0, at which point cation release was sizable. These results suggest that soils under an acid regime have already conditioned their cation exchange behavior to the current leachate, and they may have been undergoing that influence for some time.

On another point, we have been measuring the pH of snow and hoarfrost at 1350 m elevation in New Hampshire through the winter of 1971–1972. The median pH was about 3.4.

Likens: One important interface between the carbon and sulfur cycles is shown by the problem of acidity of precipitation. Currently, the pH of precipitation in the northeastern United States averages about 4 and appears to be linked to pollution of air by gaseous forms of sulfur and nitrogen, which are produced from combustion of fossil fuels. In November of 1964 the National Center for Atmospheric Research measured values as low as pH 2.0 in parts of the Northeast. Such acid rain and snow may have insidious effects on plant productivity, but we know very little about this at present. In laboratory experiments, Dr. C. C. Gordon has found that long-needle conifer species, such as white pine, produce dwarfed needles when solutions of sulfuric acid at pH <3.5 are applied by dropper to the emerging needles. When the solution is applied as a mist, pH's <4.0 result in needles that grow to only half the length of control needles. This so-called "short–long needle syndrome" apparently is prevalent in conifers of the Northeast, where pH values of this magnitude are now common, particularly during summer.

Hill: Our precipitation may well have been quite acid in the Northeast for the past 15 years; and we may be seeing the tail end of any short-term effects on soils. However, it would appear that currently there is no accelerated weathering of soils in the Northeast due to the increased acidity of precipitation.

Woodwell: Dr. Hill, would you care to comment on the effects of acid precipitation?

Hill: In the report that I referred to, which is my chief source of information on this subject, there was reference to some studies that had been done in situations in which it was possible to correlate changes in growth rate as measured by diameter of trees with calcium in the soil, and the indication was that reduction in productivity of the order of possibly 1% per year might be anticipated. They were very careful to say that this is a very difficult association to make, and I do not believe they were necessarily conclusive on this point. They thought that, in view of the risks involved and regardless of whether they could be conclusive, it was worthwhile to make a strenuous recommendation against further increases in SO_2 emission and, in fact, asked for reductions in emission.

SULFUR, NITROGEN, AND CARBON IN THE BIOSPHERE

EDWARD S. DEEVEY, JR.
The Florida State Museum, University of Florida, Gainesville, Florida

ABSTRACT

Sulfur, nitrogen, and carbon have closely analogous biogeochemical cycles, closure of which requires a biological reduction step. The cycles are coupled by the occurrence of all three elements in reduced form (as protein) in the biosphere, steady synthesis of which demands the coexistence of reducing environments, such as soil, deep water, and mud, with oxidizing water and air. On a global basis, reduction (fixation, metabolism) of C, N, and S appears to proceed at rates related as 10 : 1 : 1, respectively, although the biospheric proportions, by weight, are 554 : 7 : 1. Quantitative budgets are full of uncertainties, many of which center on unevaluated and even unproved emissions from anaerobic to aerobic environments. For example, about half the sulfur that moves through the atmosphere annually is ^{34}S-depleted and therefore biogenic and must come from the ocean in sulfide form, but emission of H_2S to the atmosphere has not been detected. Accelerated recycling of the three elements (plus phosphorus), now suspected as a consequence of pollution, can be both cause and effect of *eutrophication,* which is defined very broadly as *organic overloading.* In general, eutrophication, by increasing the proportion of anaerobic to aerobic environments, can change the mean redox state of the oceans or of the globe. The sulfur-isotope data of Holser and Kaplan[25] give evidence that the redox state has varied remarkably over Phanerozoic time.

After some hard study of the splendid review of biological cycling of atmospheric trace constituents by Hitchcock and Wechsler,[1] I have to emphasize that the gaps in our understanding of sulfur and nitrogen in nature are wider, if possible, than those related to carbon. The broad outlines of the nitrogen and sulfur cycles have been visible for a long time, but those nagging quantitative details that tell us how to balance budgets are mostly unknown. I shall have to be content, then, with some marginal notes. The limnologist's assumptions that underlie them, however, are not to be blamed on Hitchcock and Wechsler.

To make my bias explicit, I use as my first model a small lake of the sort represented by Linsley Pond. This suburban ecosystem serves as well as any to illustrate two of my most general, or more speculative, conclusions: (1) the biosphere is being eutrophicated by accelerated recycling of nutrients, and (2) this implies a significant change in the mean redox state of the globe.

As long as a lake is thermally stratified, it is neatly divided into two quite different environments. Oxidizing conditions prevail in the lighted, warmer upper waters, and, although carbon compounds are reduced there, reduction is confined to a cellular environment in close proximity to molecules of chlorophyll. Below the thermocline, on the other hand, reducing conditions prevail outside cells, but whether they prevail in the water column or only in the mud depends on the oxygen-storage capacity of the lake, a function of its mean depth. As the concentration of dissolved oxygen and the redox potential diminish seasonally toward 0 mg/liter and 0 mV, respectively, the ferrous iron, manganous manganese, and ammonium cations and the nitrate, phosphate, and bicarbonate anions appear and accumulate during stagnation.[2] Even clearer evidence of reduction appears in the form of three (or four or five) volatile substances, which, diffusing upward, may or may not be oxidized before they escape to the atmosphere. The three volatile substances, one for each of the elements of my title, are hydrogenated carbon or methane, hydrogenated nitrogen or ammonia, and hydrogenated sulfur; the fourth reduced gas is carbon monoxide, and nitrous oxide perhaps ought to be added to the list.

We know very little about the escape of these reduced gases to the atmosphere. At first thought it seems unlikely that any would escape, for they should all be rapidly oxidized and retained in solution. Ammonia, in particular, is so soluble and so avidly used as a plant nutrient that it should never reach supersaturation outside a feedlot. On second thought, gas bubbles initially composed mainly of methane rise regularly from mud,[3,4] against pressures as great as 3 atm, and, when the bubbles burst at the lake's surface, they can and do liberate gases to the atmosphere. Any mechanism that retains these gases within a bubble, such as differential solubility or adsorption on organic films, will assist in the transit of reduced substances through oxidizing water; and natural waters are notoriously rich in dissolved organic compounds—surfactants—that cause foaming.

The loss to the atmosphere of a few microbars of dissolved gases has not attracted much attention from limnologists, because the loss makes very little difference to the economy of the lake itself. What can make a difference is the tendency of ferrous iron to solubilize phosphorus. The existence of a reducing hypolimnion has long been thought to promote recycling in this restricted sense. It is not easy to quote direct evidence, for eutrophication is a complex process with multiple causation,[5] and the chemistry of "the hypolimnion" obeys complex rules that differ in force from lake to lake. Still, stagnant water has biological properties that are very different from those of flowing water, and two lakes in the same drainage system and containing the same water can differ sharply in respect to productivity and nutrient economy. One of the main sources of this kind of difference is the different amount of nutrient feedback from deep water, the vertical circulation of phosphorus and nitrate being enhanced by their tendency to accumulate in soluble form under stagnation and then to be redistributed during overturns as a massive injection to the entire lake. As a result of public changes in the basins of lakes like Erie, the importance of this form of nutrient recycling is now generally recognized. What is less obvious, but what may be of greater significance to the biosphere as a whole, is that all products of biological reduction, and not phosphates alone, will recycle at faster rates if stagnation (1) is more prolonged, (2) occurs in more lakes than before, or (3) is biochemically more intense in the eutrophic lakes we already had. I am saying that eutrophication is *organic overloading* and can expand reducing environments by overloading nature with larger amounts of a powerful reducing agent. Accelerated recycling is then both cause and effect of organic overloading.

The lake's main sources of carbon and sulfur, like those of phosphorus, are dominated by hydrologic throughflow. Sulfate from an oxidized environment flows through in such quantities as to mask a limnological process—sulfate reduction—that is just as important from the standpoint of this conference as photosynthetic fixation of carbon. We knew that it was important, but the first quantitative demonstration waited for the availability of isotopic tracers. Sulfide sulfur is depleted in ^{34}S with respect to sulfate, and in 1960–1961 Nakai proved the existence of fractionation, i.e., of an enrichment–depletion cycle, in the deep water of Linsley Pond.[6] From the enrichment of the heavier isotope in the remaining sulfate when ferrous sulfide was precipitated in the mud, and from mass-balance considerations, Nakai and I calculated that about 1 mg of sulfur was annually reduced per square centimeter of lake surface. As the figure is nearly a tenth of the estimated carbon fixation (13 mg C cm^{-2} $year^{-1}$ from Riley's old figures), we thought it must be too high. But when Stuiver[7] in 1964 injected radiosulfur, ^{35}S, into the hypolimnion of Linsley Pond and found that it all went into mud sulfide and stayed there, it turned out that 1 mg S/cm^2 is the figure for 4 months of summer stagnation and that the annual fixation may be two or three times as much. Meanwhile, in 1962 we acquired some data on a more special lake, meromictic Green Lake at Fayetteville, N. Y.,[8] that far surpasses Linsley Pond as a microbial sulfur–redox system (Table 1).

Green Lake[9-13] is permanently stagnant below 20 m. At the top of the monimolimnion, where H_2S diffuses up from below, is a port-wine-colored bacterial plate, the color belonging to the photosynthetic sulfur bacterium *Chromatium vinosum,* although the green bacterium *Chlorobium phaeobacteroides* is actually more common. About 83% of the primary carbon fixation in this lake is by these sulfur oxidizers.[14] However, what keeps them in business is free H_2S, made anaerobically in the depths by sulfate reducers of the *Desulfovibrio* type. At its maximum, near bottom in 52 m, sulfide sulfur reaches a concentration of nearly 40 mg/liter, diminishing upward to zero at the chemocline (Table 1). None is detectable in the upper lake, of course, but the ^{34}S ratio in surface-water sulfate is depleted below the ratio in the inlet water.

TABLE 1

LIMNOLOGICAL AND ISOTOPIC DATA[8] FROM GREEN LAKE, FAYETTEVILLE, N. Y., JUNE 30, 1962

			Sulfur, mg/liter		$\partial^{34}S$ (per mil)			
Depth, m	Temp., °C	O_2, mg/liter	SO_4^{2-}	S^{2-}	SO_4^{2-}	S^{2-}	CO_2, ml/liter	$\partial^{13}C$ (per mil)
0	21.52	5.97	446	0.0	+23.7		55.7	−7.0
18	9.35	5.50	449	0.0	+24.4		109.8	−11.2
20	7.91	2.70	455	6.7	+25.3		125.9	−13.7
25	7.68	0.65	446	18.4	+27.5	−28.8	144.8	−17.0
35	7.70	0.0	444	25.4	+28.2	−26.8	147.9	−16.0
45	7.85	0.0	417	34.3	+31.3	−26.3	166.1	−17.8
52	7.90	0.0	422	39.4	+30.0	−25.0	164.3	−20.1
Inlet			298	0.0	+24.7			

This depletion confirms what the vertical gradients also show, that the lake is a trap for total sulfur but loses ^{34}S. Isotopic fractionation between sulfide and sulfate is maximal, averaging 57 per mil, in the monimolimnion. But light (^{32}S enriched) sulfide is reoxidized in the upper lake (the mixolimnion), and export via the outlet results in a slight net loss of heavy ^{34}S.

We noted that the model suggested by these data is a reflux system with a leak near the top. We also compared the lake to a salt dome, where bacterial production of free sulfur preferentially removes ^{32}S from seawater, and the associated sulfate deposits[15] are strongly enriched in ^{34}S. There are coupled biological processes that fractionate the carbon isotopes,[16] and Green Lake carbonate, like the carbonate in the caprock of a salt dome, is strongly depleted in ^{13}C.

Green Lake is certainly not a typical lake. It owes its meromixis to deep seepage of exceptionally saline groundwater, entering a basin of unusual shape and depth[17] that was formed as the plunge basin of a late glacial waterfall. It differs from more ordinary lakes in its initially high sulfate content—about a hundred times that of Linsley Pond. Moreover, apparently because there is so much more sulfur than iron, H_2S is free to diffuse upward, and the mud of Green Lake is not a trap for sulfide in the form of FeS, as Linsley Pond is. Neither lake appears to liberate sulfide to the atmosphere, the "leak at the top" of Green Lake being an outlet to water, not to the air. So the main conclusion of my limnological excursion is not what the atmospheric scientists may have hoped. If massive quantities of sulfur enter the atmosphere from reduced hypolimnia, enabling geochemists to balance the global sulfur budget,[18] I cannot prove it and do not claim it. All I claim is that the metabolism of sulfur, on an areal basis, can be about a tenth as active as the metabolism of carbon; but the intensity of that metabolism has not been appreciated because it is screened from our view by an oxidizing environment.

As to nitrogen, I can say very little and nothing that is novel, for the limnological chemistry of nitrogen is beset with quantitative uncertainties. The dominant reservoir, as for soil nitrogen, is of course the N_2 of air. Nowadays there is reason to suspect that airborne nitrate from fertilizer and automobile exhaust has much to do with the eutrophication of lakes. Insofar as there is steady-state exchange between biosphere and atmosphere, the closure of each redox cycle depending on reduction steps performed anaerobically,[19] one would expect a quantitative expansion of anaerobic environments resulting from organic overloading to intensify the recycling of nitrogen as of sulfur and phosphorus. But intensified recycling on a regional scale should enhance the rates of emission of reduced substances to oxidized environments, e.g., the emission of ammonia and nitrous oxide to the atmosphere, and these emissions are so hard to detect, when diluted into enormous oxidized reservoirs, that we have exceedingly little reliable information. (More or less identical considerations apply, of course, to the emission of CO, CH_4, NO, H_2S, SO_2, and polythionates.) Limnologists have been exclusively concerned with the import of nitrogen and with its internal cycling within the lake, and they have contributed almost nothing to the export side of the equation. Most export is of course as nitrate in surface outflow.

I have pointed out that the biosphere,[20] quantitatively dominated by woody plant tissue, can be regarded as a chemical compound with the empirical formula

$$H_{2960}\,O_{1480}\,C_{1480}\,N_{16}\,P_{1.8}\,S$$

This tells us that the N : S ratio by atoms averages 16, the C : N ratio is 92.5, and the C : N : S proportions are 1480 : 16 : 1. If we cannot compare budgets of C, N, and S, we can at least look at relative global mobilities (Table 2). Mobility of these three elements is entirely biogeochemical, a function of their redox properties, and has little to do with relative geochemical abundance or even with the present sizes of their mobile reservoirs.

TABLE 2

CARBON, NITROGEN, AND SULFUR: MOBILE RESERVOIRS, METABOLISM, AND BIOSPHERIC COMPOSITION

	C	N	S
Mobile reservoir, g/cm$_e^2$	7.03	720	240
Metabolism, mg cm$_e^{-2}$ year^{-1}	15.3	1.5	1.5
Biospheric composition, g/g S	554	7	1

If we take the net fixation of carbon on earth as 78 × 10^9 tons/year and divide by the area of the earth, carbon metabolism comes out at 15.3 mg $\mathrm{cm_e^{-2}}$ $\mathrm{year^{-1}}$. For nitrogen assimilation, I use the Hitchcock and Wechsler figure,[1] 7.9 × 10^9 tons/year, even though I am cited as the authority for the terrestrial half, but the number really comes from Rodin and Bazilevich.[21] Nitrogen is then a tenth as mobile as carbon on an areal basis, 1.5 mg $\mathrm{cm_e^{-2}}$ $\mathrm{year^{-1}}$.

For sulfur, I will use a figure which Hitchcock and Wechsler regard as very high but which seems to me about right. Lloyd[22] has been looking at the ^{18}O : ^{16}O ratio in seawater sulfate and finds it so grossly out of equilibrium with the ^{18}O of the oxygen as to imply an annual reduction within the ocean of 7.8 × 10^9 tons of sulfur, reoxidation of which would yield the observed value of $\partial\ ^{18}$O in oceanic sulfate, 9.7 per mil. The argument is indirect, and the data are scanty, but I cannot help noticing that on an areal basis the metabolism of sulfur comes out at 1.5 mg $\mathrm{cm_e^{-2}}$ $\mathrm{year^{-1}}$, about the same as on the floor of Linsley Pond and about the same as the metabolized nitrogen. It is now generally accepted[18] that about half the annual sulfur budget of the atmosphere must come from the sea in nonsulfate form. If Lloyd's figures are right, only about 1% of the reduced marine sulfur need reach the atmosphere by any mechanism to make the budget balance.

So, provisionally, we can set the relative mobilities of metabolized C : N : S as 10 : 1 : 1. These ratios are very different from the proportions occurring in the biosphere, 554 : 7: 1 (by weight); and if we look (Table 2) at the mobile reservoirs from which these proportions are drawn at these relative rates, we find them not even in the same order of rank. Carbon has the smallest mobile (atmospheric plus marine) reservoir, 7.03 $\mathrm{g/cm_e^2}$; sulfur is next with 240 $\mathrm{g/cm_e^2}$; and nitrogen has an enormous reservoir, 720 $\mathrm{g/cm_e^2}$. Coupling between these reservoirs is clearly very nonlinear.

The problem of the sulfur balance to which I have been alluding is the old problem of the excess sulfate in continental runoff. A large fraction of the sulfur in rainwater clearly comes from industrial pollution, i.e., from the combustion of fossil fuels and the pollution of rivers by spent sulfuric acid. Another large fraction certainly comes from sea spray, as chloride does, although there are some second-order arguments[23] about the S : Cl ratio to be used in estimating how much rainwater sulfate is marine in this sense and how much is excess. The largest fraction—about half the atmospheric budget, according to Kellogg et al.[18]—presumably also comes from the sea, but its isotopic ratio, now measured in several places, shows convincingly that its origin was not in sulfate form. It is this ^{34}S-depleted fraction that is now presumed to be biogenic, of microbial origin in a reducing environment, as suggested many years ago by E. J. Conway.

Apart from the lack of direct evidence of H_2S emission on any scale, let alone the massive scale required, there are two main sources of uncertainty in this picture. One is the fact that much industrial sulfur is as depleted in ^{34}S as any other sulfide, whereas fertilizer sulfate is enriched; the isotopic label does not label *biogenic* sulfur unambiguously. The other source is in the original figures for the sulfur in continental runoff, which mainly turn out[1] to have been jotted down on foolscap by contemporaries of Sir Humphrey Davy. So far as these can be brought up to date, they suggest (to Berner[24]) that Europe and North America have far more excess sulfur than the unindustrialized continents. Nevertheless, Berner is among those who agree that there is a great deal of excess sulfur in circulation and that most of it is biogenic. He argues, however, that the biogenic fraction has been increasing in the Northern Hemisphere along with the industrial fraction owing to excessive *organic* loading of the seas around Europe and North America.

Welcoming Berner to the Institute of Ecology, we note that an expansion of anaerobic environments accelerates the rate of recycling of all elements whose cycles involve a biological reduction step. Eutrophication is then a general phenomenon, potentially affecting the entire biosphere.[20] It makes little difference, at least in the early stages of acceleration, whether the limiting nutrient is seen as phosphorus, carbon, nitrogen, or sulfur. In a lake, excess phosphorus accelerates carbon fixation, shifts the phytoplankton composition in favor of nitrogen-fixing blue-green algae, promotes anaerobiosis in deep water, and so accelerates the formation of ammonia and sulfide. On land, the excess nitrate and sulfate in rainwater and the direct absorption of excess carbon and sulfur dioxide can accelerate organic production and nitrogen fixation; and excess nutrients exported to sea, whether or not they include particulate or dissolved carbon compounds, will eventually eutrophicate the oceans too.

I have now to remind myself that we do not *know* that the biosphere is increasing. If it is, we can guess that it will not increase indefinitely, despite accelerated recycling. Some one of the newly accelerated rates will become rate limiting on the rest, although I for one have no idea which one it will be.

In principle, these ideas are testable in a number of ways. Every quantitative deduction I can think of—such as the prediction that emissions of carbon monoxide and nitrous oxide from the ocean should be increasing—stumbles over a gross inadequacy of analytical data. One set of predictions, having to do with the fractionation of nitrogen isotopes in nature, I intend to test in my own laboratory. You will doubtless think of others. Meanwhile, there is a sort of historical postdiction, posed by Holser and Kaplan's data on $\partial^{34}S$ in marine sulfates,[25] that I find fascinating (Fig. 1).

We have had to give up H. G. Thode's attractive idea, on the basis of a first look at these data, that isotopic fractionation of sulfur began with the first living organisms. Changes in the volume of the oceans might account for these remarkable variations, but that idea always falls before the razor of William of Occam, alias Karl Turekian. There could have been changes in the mean temperature of the oceans, but, in the simple form hinted at by Hitchcock and Wechsler,[1] a theory of temperature dependence seems to predict minimal

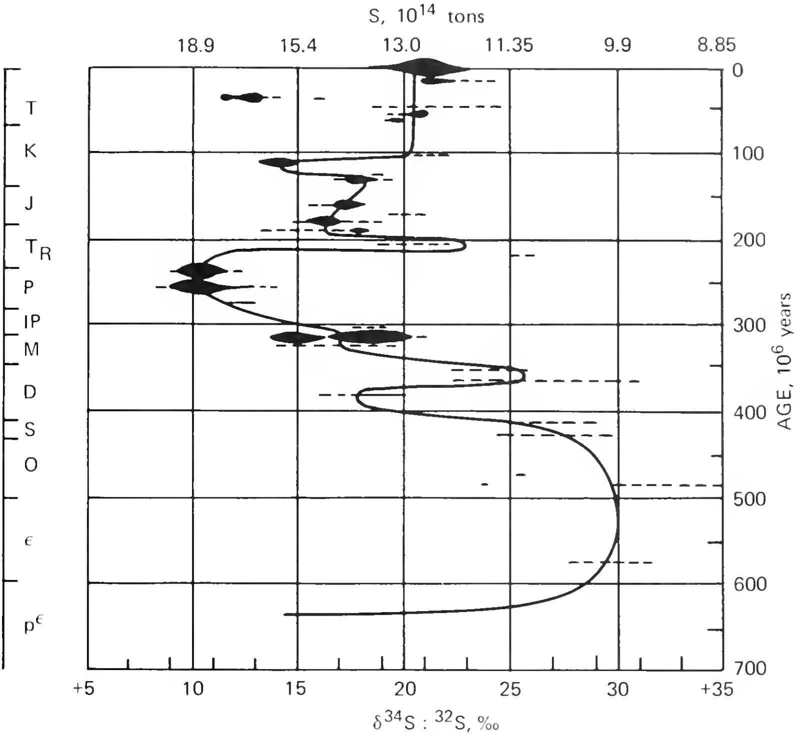

Fig. 1 Sulfur-isotope age curve, from Holser and Kaplan.[25] Computed total quantities of oceanic sulfur, based on an assumed constant oceanic volume, have been added by Hitchcock and Wechsler.[1] (After Hitchcock and Wechsler.[1])

temperatures in the Permian and Cretaceous periods, which I find counter-intuitive.

Holser and Kaplan[25] suggested that there is a shifting balance between the weathering of sulfur from sediments, which they assume to be chiefly shales, and the deposition of sulfide in the sediments: at times when more light sulfur leaves the ocean than enters it, the concentration of sulfur in the ocean falls, and the ∂ ^{34}S of the remaining sulfate rises. (The scale showing the quantity of sulfur has been added to the diagram, Fig. 1, by Hitchcock and Wechsler.) This, too, is an oversimplified model because it neglects evaporite sulfur, assumes an ocean of constant volume, and makes predictions about the oxygen content of the ocean–atmosphere system which are hard to verify. If we notice that, during high rates of deposition of ^{32}S and sulfide, the mean redox state of the ocean is lower so that black shales can be both formed and preserved in the open ocean, we are suggesting oscillation in the relative proportions of anaerobic environments. If that suggests intensified recycling of biological elements, there are interesting implications for the *terrestrial* ecology of the Devonian, the

Carboniferous, the early Triassic, and the early Tertiary periods. By comparison with these "normal" times (normal with respect to $\partial\,^{34}S$), when most of the interesting events seem to have taken place on land, the Ordovician period seems to have had too much anaerobiosis and recycling, and the Permian and Cretaceous too little.

For a final comment on recycling, in language appropriate to the grandeur of the process, I turn to Bidder.[26] Nearly 50 years ago that great student of sponges noticed how *Euplectella,* the Venus's flower basket, lies on the floor of the deep ocean, athwart the North Atlantic Deep Water on its way to becoming the Equatorial Divergence. "Food is brought to them," he said, and "waste is taken away. For them in their eternal abyss, with its time-like stream, there is no hurry, there is no return. Such an organism becomes a mere living screen between the used half of the universe and the unused half—a moment of active metabolism between the unknown future and the exhausted past."

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PHASE PHENOMENA IN THE CALCITE–SEAWATER SYSTEM

ROBERT C. COOKE
Department of Oceanography, Dalhousie University, Halifax, Nova Scotia

ABSTRACT

The movement of calcite from its source of production in surface waters to its point of retention in the sediment is affected by both chemical and physical factors. Experiments in which both pressure and composition were varied in the calcite–seawater system show that definite stability boundaries exist and that the lysocline is at least partly a function of the presence of magnesium in both solid calcite and seawater. The concentrations of calcium and magnesium in seawater, or its salinity, also determine the pressure beyond which calcite must dissolve and the composition of the solid calcite required for it to be in steady state in the sea.

The flux of carbon dioxide in and out of marine sediments occurs in three stages. The first stage is the mass transport of the gas through the boundary layer at the sea surface and the associated processes of hydration and ionization. The second stage is the incorporation of the resultant carbonate into the hard and soft parts of plants and animals by biochemical means and the subsequent release of this material by decay and disintegration. The third is the race between sedimentation and dissolution of the calcite and aragonite produced by organisms in the waters above the sediment. This paper concerns itself with the flux of carbon dioxide to the sediments as carbonate minerals and from the sediments as dissolved carbonate salts.

The distribution of calcium carbonate in the sediments could be explained as a function of primary productivity and current patterns if the carbonates were carried directly to the sediment by currents and gravity. This is not the case (see references of Arrhenius,[1] Bramlette,[2] Turekian,[3] Cloud,[4] and others) because the solubility of both calcite and aragonite is dependent upon temperature, salinity, depth, and circulation pattern. I will attempt to describe several of these factors in relation to the carbonate system and solid calcite and will then describe research directed at one aspect of the general problem of the change of calcite solubility with variation in pressure and seawater composition.

A general description of the solubility of calcite in seawater should explain both the removal of carbonate minerals from fresh sediment at great depths and the sharp reduction in the carbonate composition of water near the 4000-m depth. The basic process is dissolution, but the reasons for its discontinuous effect are complex. If we assume that dissolution proceeds because the chemical potentials of the components of carbonate minerals in the sea are less in solution than in the solid state, then dissolution should be a continuous process with increase of pressure. However, dissolution is observed not to increase linearly with depth. Solubility of calcite as a function of seawater composition alone has been investigated by many workers, notably by Weyl[5] and Pytkowicz[6-8] in a number of articles between 1964 and the present. The behavior of foraminiferal tests in seawater has been investigated by Berger.[9-12] The effect of pressure has been examined by Pytkowicz,[7] Cooke,[13] and Peterson.[14] Most relevant to the experiments described herein are Peterson's[14] 1966 article and Berger's[9] in 1967. These articles indicated that the effect of pressure, perhaps alone, might be sufficient to maintain the lysocline, a level in the ocean below which dissolution must proceed and above which dissolution does not proceed.

EXPERIMENTATION

Construction of the pressure apparatus shown schematically in Fig. 1 was complete in the fall of 1969. This device allows seawater of a predetermined pH and salinity to flow at a controlled and measured rate through a column of finely divided analytical-grade calcite.

The kinetics of the dissolution or precipitation of calcium carbonate are relatively slow; if the calcite column length is too short or the seawater flow rate too rapid, the system will not be able to achieve steady state and the observed gain or loss of total carbon dioxide in the seawater that has passed through the reactor will be a function of flow rate and solubility and not of solubility alone. As insurance that observations were being made of calcite solubility only and not of kinetic behavior as well, the experiments were run with the seawater flow rate approximately 25% of the rate necessary to exceed the dissolution kinetics of the system.

The analytical system is shown schematically in Fig. 2. Seawater passing through the calcite column at 0.90 ml/min leaves the high-pressure system through a valve and enters a manifold, after which it is pumped by precision pump (Buchler) to an acid-filled decomposition flask at 0.77 ml/min. The balance of the flow escapes from the manifold through an RGI flowmeter, and adjustment according to the flowmeter readings allows a regulated flow of seawater to pass through the reactor. The precision pump used for the steady supply of reacted seawater to the decomposition flask showed a variation of less

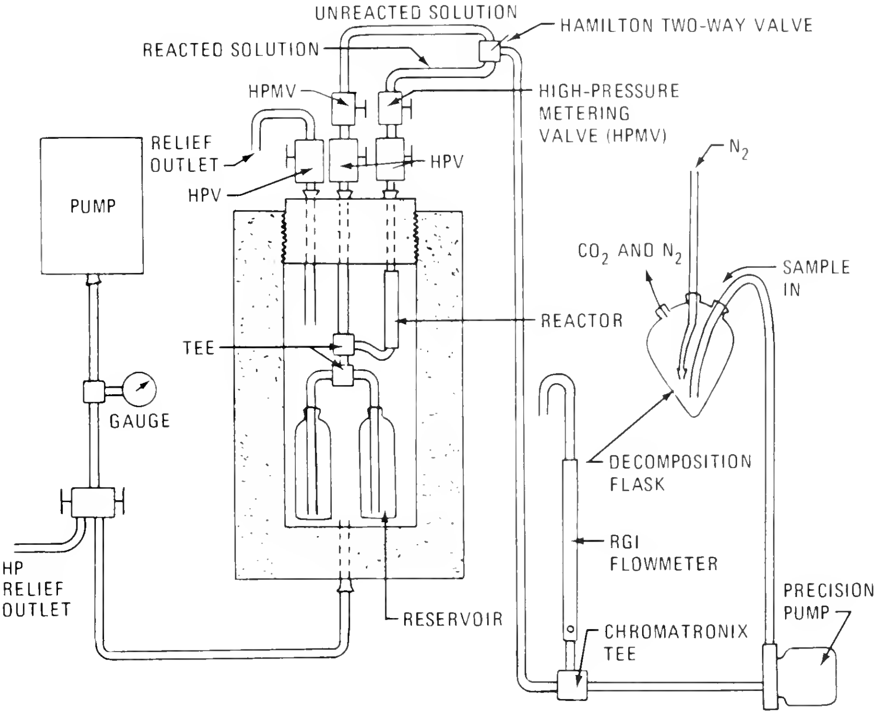

Fig. 1 Pressure system for calcite dissolution.

than 0.5% per day, the calibration being against the flowmeter connected to the manifold.

Standard carbonate solutions were prepared by adding appropriate amounts of K_2CO_3 to each of six vessels containing known amounts of CO_2-free water. The K_2CO_3 concentrations were adjusted to span the expected total CO_2 values for Sargasso Sea water. The carbonate standards were protected against atmospheric CO_2 by fitting them with tubes filled with Ascarite. In use, the standard solutions were pumped to the decomposition flask in the same manner as the seawater. A linear relation was obtained between analyzer output in counts per second and total CO_2 in the standards. Seawater or standard solutions sent to the decomposition flask entered a solution with a pH of approximately 0.4 and thus had all their carbonate-system components converted to CO_2. Liberated CO_2 was swept from this acidic solution by a controlled flow of pure nitrogen entering the solution through a fritted tube. The resultant mixture of nitrogen and CO_2 then flowed to the CO_2 analyzer (Beckman Model 15).

The experiments were designed to investigate the dissolution of nearly pure calcite in seawater under pressures typical of the deep sea. Representative seawater for these experiments was collected from 2000 m in the Sargasso Sea,

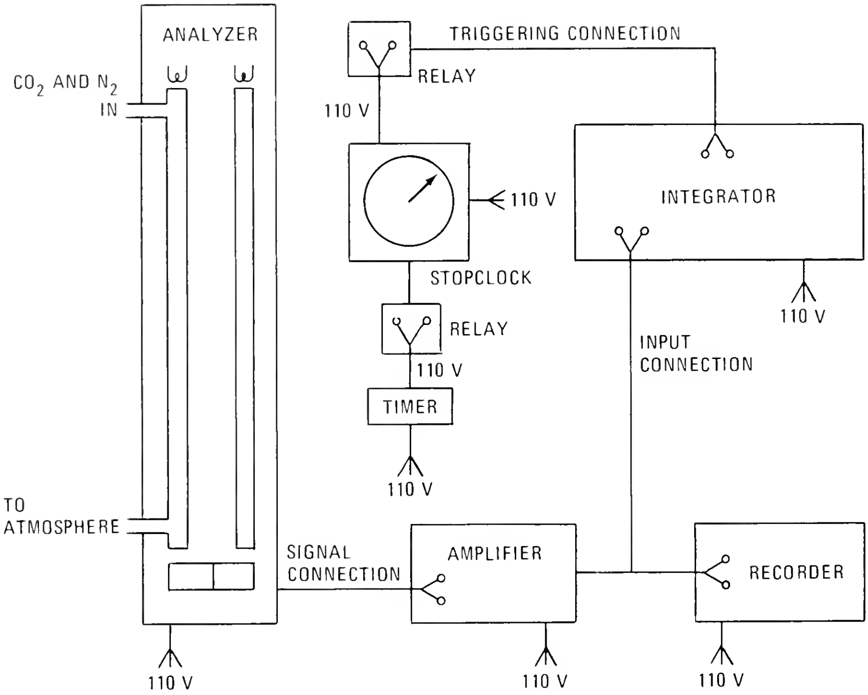

Fig. 2 Analysis system.

approximately 80 miles north of Bermuda. Artificial seawater and ion-deficient seawater were also used (Lyman and Fleming[15]).

Total CO_2 in seawater, both before and after exposure to calcite in the reactor, was determined by taking the seawater from the pressure vessel through alternate valving (Fig. 1). Once background total CO_2 was measured in seawater not in contact with the calcite, the total CO_2 in calcite-exposed seawater was determined at a number of pressures. Information in the figures is presented in terms of concentration of total CO_2 in exposed seawater vs. pressure. The total CO_2 concentrations in the exposed seawater, relative to the unexposed seawater, is indicative of precipitation, dissolution, or steady state within the calcite–seawater system. These three processes were all observed and were functions of pressure and composition.

In the first experiment, seawater of 35.5‰ salinity and pH of 7.985, with total CO_2 of 2.247 millimoles/liter, was passed through the calcite column in the system described in the preceding paragraph. At moderate pressures (10 to 334 atm), precipitation took place upon the calcite surfaces within the column, and the total CO_2 of the effluent seawater was diminished by removal of carbonates from solution. The schematic recorder trace for this process is shown in Fig. 3. In Fig. 3, seawater is passing through the reactor after having laid down a

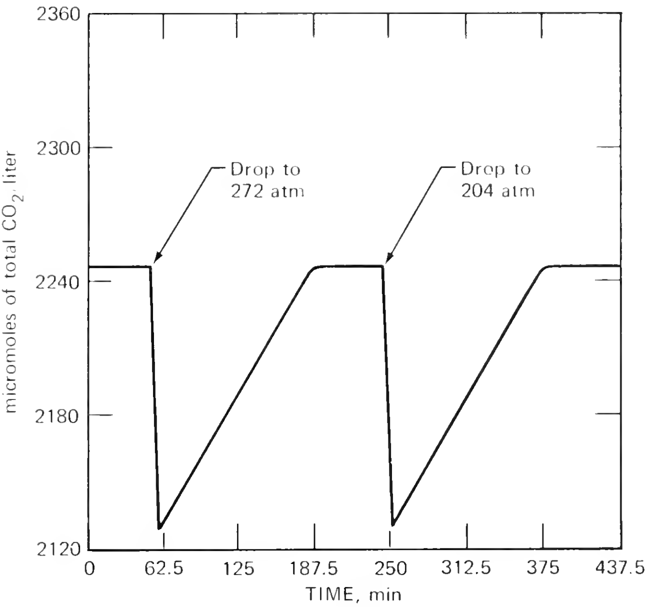

Fig. 3 **The effect of pressure drop on steady state.**

precipitate on all the available analytical calcite surfaces therein. The system is in steady state at the left border of the figure, as total CO_2 of the incoming seawater is the same as the total CO_2 of the effluent seawater. If the pressure is now dropped quickly from some nominal value below 334.1 atm to a lower value, precipitation begins upon exposed calcite. This action results in a drop in the total CO_2 of the effluent seawater, and 125 min are required to complete the covering of the older phase with a new phase that is stable under the imposed conditions of pressure, temperature, and seawater composition. If the pressure is again dropped after the 125-min period necessary to lay down a stable phase, a new phase will be formed in the same manner. Thus, for repeated drops in pressure, with seawater flow rate held constant and steady state reachieved before each new lower pressure is set, the original calcite particles containing 100 ppM magnesium are coated with one layer after another of a precipitate whose surface is stable at the pressure obtaining during its formation.

If the operations are performed in reverse order, with the pressures raised in steps instead of being dropped, completely different results are obtained (Fig. 4). Starting at a low pressure, with the system in steady state and, for simplicity, only the phase stable at that pressure present on the original calcite particles, an increase in the pressure to any point less than 334.1 atm will cause a rapid dissolution of the precipitated phase followed by an irregular return to steady state over a 150- to 180-min period. The same results are obtained if the pressure is raised again after steady state has been achieved for the second time,

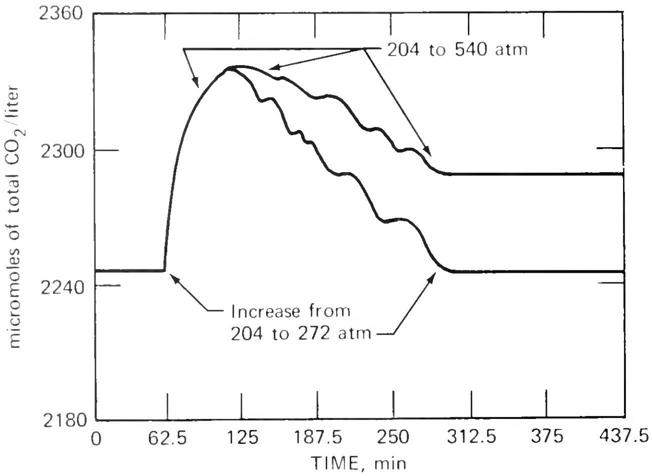

Fig. 4 The effect of pressure rise on steady state.

and the process can be repeated as many times as the upper pressure boundary (334.1 atm) will allow. In this case the size of the pressure differential determines the rate of removal of the previously precipitated phase, because the solubility of the phase increases markedly with pressure. The greater the pressure jump, the more rapidly the previously stable phase is dissolved and removed. It is quite important to comment at this stage that the analytical calcite itself has not undergone any dissolution. At no time while the pressure is below 334.1 atm does the system fail to come back to steady state after a pressure change. If any net dissolution were proceeding, a steady state could not be achieved. What if the pressure is raised above 334.1 atm? When the pressure is raised somewhat above this value, there is a rapid loss of newly unstable material which is followed by a return to a total CO_2 value in the effluent seawater which is clearly above background and thus due to the dissolution of the analytical calcite. Thus, above 334.1 atm in this particular system, steady state can no longer be achieved because the composition of the basement calcite is fixed at 100 ppM Mg^{2+}, and a more stable, or less soluble, calcite, containing less than 100 ppM Mg^{2+}, cannot precipitate upon the original surface because the original surface must dissolve. These observations will be discussed further in the following paragraphs.

Analytical calcite showed dissolution only above a pressure of 334.1 atm in Sargasso Sea water, but it was able to achieve steady state with this water at any lower pressure. When the crossover pressure is approached from above in the same system and total CO_2 is measured at selected pressures above 334.1 atm, the system behaves as shown in Fig. 5. This experiment was performed many times over a period of 15 months and gave the same results as long as the same seawater and calcite were used. A line of best fit was drawn through the points

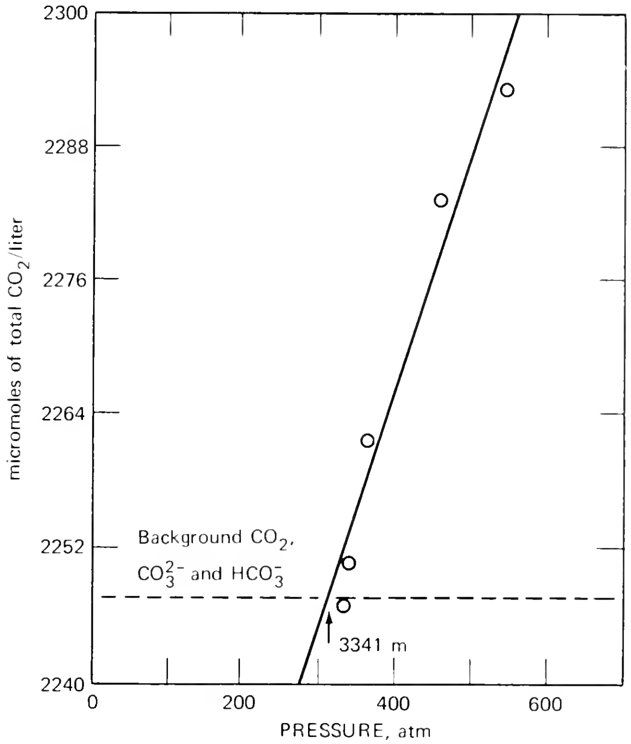

Fig. 5 Dissolution behavior in Sargasso Sea water.

relating pressure to concentration (or total CO_2). The pressure at which this line intersects the background total CO_2 line is called the lysocline pressure for the particular system.

Figure 6 shows the results of the same experiment using artificial seawater of 33.5‰ salinity, a pH of 8.136, and a total CO_2 of 2.289 millimoles/liter. The lysocline pressure is somewhat less, although the intersection has been shifted to the right by the higher total CO_2. Real comparisons between experiments require very similar values of the total CO_2 for establishing the lysocline pressure.

Figure 7 shows the results of the same experiment using Sargasso Sea water diluted 1 : 1 with distilled water. The 18.7‰ salinity mixture was equilibrated with air at 770 torrs and 23°C before use. Because the range of standards did not extend low enough to include the total CO_2 of this seawater, the ordinate is expressed in observed counts per second. Here the lysocline pressure has been depressed to 238.7 atm, indicating that the aggressiveness of seawater in dissolving calcium carbonate is dependent upon its salinity. This follows from the expression of salinity as a measure of the calcium and magnesium concentrations of the water.

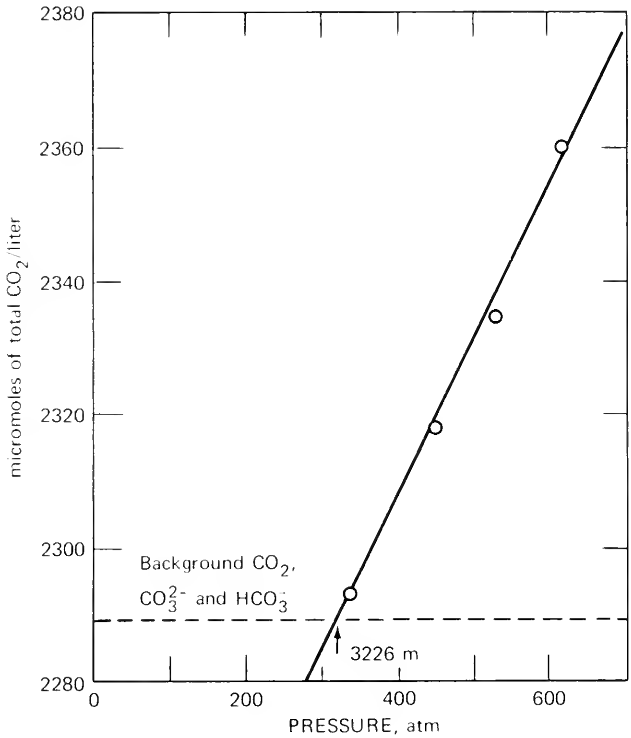

Fig. 6 Dissolution behavior in orthodox artificial seawater.

Figure 8 represents a class of experiments in which artificial seawater compounded in accordance with Lyman and Fleming,[15] but with sodium ion replacing magnesium ion, was used as the fluid medium. The results shown indicate that a profound change in the system behavior has occurred. No precipitation could be secured at any pressure. Dissolution began immediately once the artificial seawater began to flow, and the solubility of the calcite increased nonlinearly with increase in pressure. Thus the presence of magnesium in solution is necessary for the maintenance of a lysocline. Further experiments showed that the introduction of magnesium into the magnesium-free seawater produced the effect of the lysocline. A further experiment which demonstrated that the precipitated phases do in fact contain magnesium in proportion to the pressure at which they are stable was then performed. Results are shown in Fig. 9. Analytical calcite within a column was coated with a precipitate laid down from seawater at a selected pressure and then removed from the column, dissolved in dilute HCl, and analyzed for magnesium by atomic absorption. Figure 9 shows the results of these incorporation experiments, which were done at pressures of 142.9, 287.2, and 389.9 atm. In the first two, precipitation was allowed to proceed to completion (240 min); no precipitation took place in the

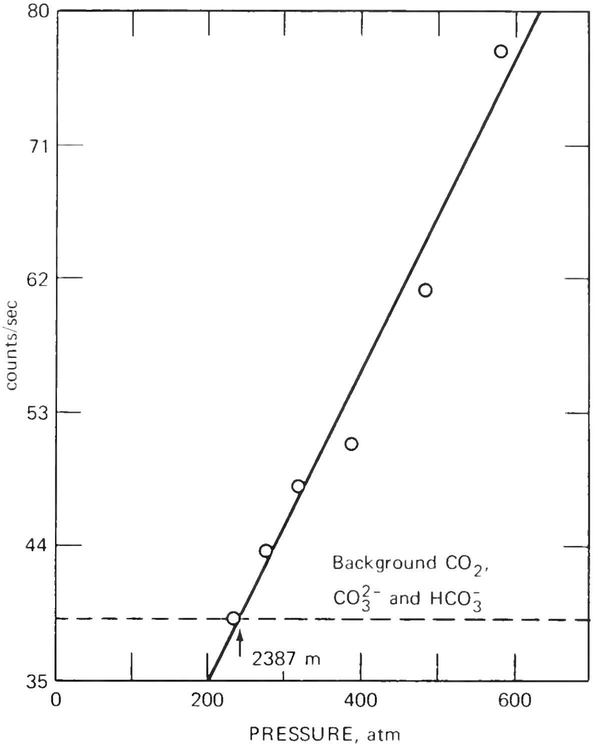

Fig. 7 Dissolution behavior in 18.7‰ seawater.

third experiment. Ratios of calcium to magnesium as plotted in Fig. 9 were the amount of calcium present in the calcite column by weight divided by the amount of magnesium present in the column by analysis. The amount of magnesium incorporated by the uptake of a given quantity of seawater without any incorporation of magnesium through precipitation should approximate the amount taken up in the run made at 389.9 atm. In a comparison of the incorporation of 389.9 atm with the value that would result if no precipitation took place, a reactor containing 1.7020 g of calcite was allowed to become saturated with Sargasso water (this same reactor, containing the column of calcite, was used in all the experiments). The increase in weight that resulted from this saturation was 3.01 g. This amount of Sargasso water would be expected to increase the amount of magnesium in the reactor by 4.01 mg, in good agreement with the experimental value for the highest pressure sample. The Ca/Mg ratio for the saturation sample was 169.8, compared with 168.4 in the highest pressure sample. Thus the incorporation of magnesium in the calcareous precipitated materials is inversely proportional to the pressure at which they are formed.

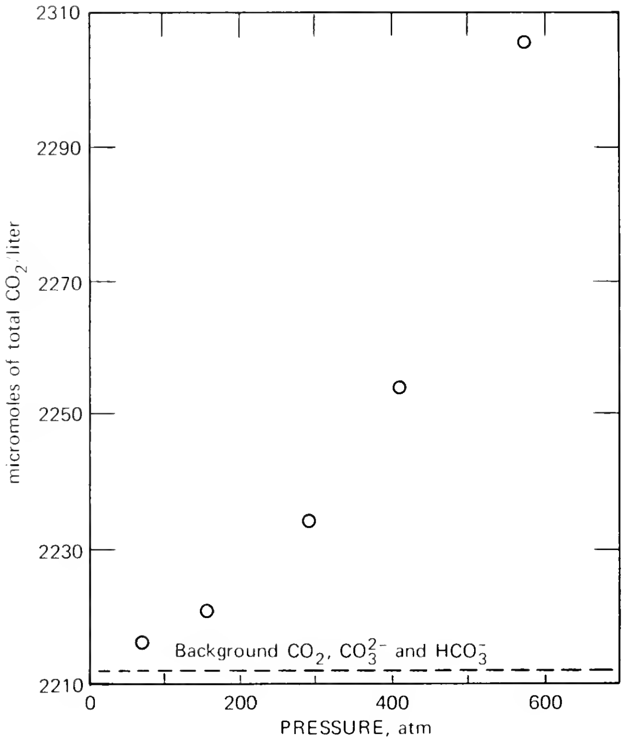

Fig. 8 Dissolution behavior in artificial seawater without Mg^{2+}.

It was further observed that, with the temperature and pressure fixed, the system was able to reach steady state because the composition of the solid solution of $MgCO_3$ and $CaCO_3$ in contact with seawater was a function of the pressure. With seawater composition changed and the salinity less, less pressure was needed to exceed the lysocline pressure. In another series of experiments, with magnesium concentration 125% of normal in the artificial seawater, the lysocline pressure was 366.3 atm. With the magnesium concentration 67% of normal, the lysocline pressure was 273.0 atm. The chemical potential of an ion in solution must be the same as the chemical potential of the same ion in the solid if steady state is to be achieved. The phase rule of Gibbs was applied at this point to systematize the observations.

If the system is assumed to contain $CaCO_3$ and $MgCO_3$ and water as components and these are distributed between two phases, solid and liquid, then there are three independent variables in the system, the temperature, the pressure, and the composition of either liquid (the seawater) or solid (the calcite containing magnesium). With the pressure fixed, the temperature fixed, the composition of the seawater the same throughout the calcite reactor and the system in steady state, experimentation shows that the system has reached

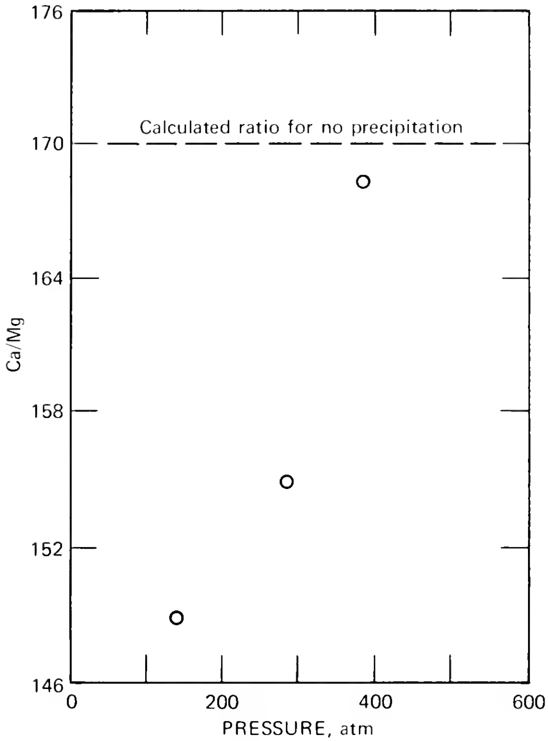

Fig. 9 Calcium/magnesium in exposed calcite.

steady state because the composition of the solid solution in contact with the seawater has changed. The solid-solution composition is thus the dependent variable. This need not be so, since the composition dependence can be shared between the solid solution and the liquid solution, but in steady-state systems of this type the composition of the liquid solution is fixed.

If the pressure and temperature are fixed but the seawater composition is changing, the solid-solution composition must change accordingly if steady state is to be achieved.

If the seawater composition and the temperature are fixed, a change of pressure requires a change in solid-solution composition for the establishment of a new steady state.

If the solid-solution composition is changed, with the seawater composition and the temperature fixed, the pressure must be changed to maintain steady state. If one or more of the independent variables is not altered, then the process that results from changing the solid-solution composition will proceed to completion. That is, if the solid solution is higher in magnesium than required for steady state at a given temperature, pressure, and seawater composition, then the pressure must be reduced, the temperature increased, or the magnesium-ion concentration increased, or any combination of these, to bring the system to steady state and prevent the disappearance of the stable phase by dissolution. If the solid solution is lower in magnesium than is required for steady state at a given temperature, pressure, and seawater composition, then the pressure must be raised, the temperature dropped, or the magnesium concentration in liquid solution decreased, or all of these, to bring the system to steady state and prevent the formation of a stable higher magnesium phase by precipitation.

The effect of temperature is now being investigated. It is a classical variable in this type of thermodynamic analysis and is not expected to behave unusually, but this remains to be seen.

In the natural system, if these observations are correct, the temperature and the pressure and the seawater composition determine the depth at which calcites of different composition can be stable, where they will become unstable, how rapidly the differing compositions will dissolve, and what range of solid-solution compositions can exist in the sea. As the calcite—seawater system is only in equilibrium or steady state when the chemical potential of each component in the one phase is equal to the chemical potential of the same component in the other phase, the ultimate analysis of the system will lie in determining its phase relations.

Chemical-reaction boundaries are only part of the problem of explaining calcareous sediment distribution. The distribution is a function of biological activity at the surface, oceanic circulation and local turbulence at all depths and the time period during which postdepositional changes can occur, and all the other factors discussed in this paper. This combination of physical and chemical effects will determine the amount of CO_2 as carbonate minerals reaching and remaining in the sediments, and the amount dissolving and returning to the oceanic carbonate system.

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DISCUSSION BY ATTENDEES

Kilham: I have studied the magnesium and strontium contents of deep-sea bivalve mollusks from 1000 to 5000 m in the Atlantic. Generally, I found that the amount of magnesium in the shells decreased with increasing depth. The same was also true of strontium. It is important to note that all the shells were aragonitic.

Cooke: Strontium is taken up in aragonite to a greater extent than it is in calcite—magnesium taken up in calcite. I did experiments on strontium and found no discernible result by changing strontium in a calcite system. Obviously, the number of experiments that would follow this sort of thing are legion, but aragonite has to be looked at as well. It may be that much the same thing exists in that case—on the other hand, if there is no inclusion or incorporation of an atom in the lattice of aragonite which raises its solubility, then the lysocline for aragonite would perhaps have a completely different source.

PARTICULATE AND DISSOLVED ORGANIC CARBON IN THE OCEANS

GORDON A. RILEY
Institute of Oceanography, Dalhousie University, Halifax, Nova Scotia

ABSTRACT

Total nonliving organic carbon in the oceans averages 1 mg C/liter, more or less, and totals 10^{12} metric tons or more in all the world's oceans. This is estimated to be of the order of 100 times the carbon content of living organisms in the sea. The preponderance of nonliving material is indicative of gradual accumulation and a long residence time, suggesting that much of the organic matter is virtually unusable biologically. However, recent evidence suggests that perhaps 1% or a little more consists of free amino acids and other biologically labile substances that are recycled more rapidly. These substances can be used for growth of small heterotrophic algae and bacteria that then serve as a food supply for filter-feeding animals. Bacterial action and certain physical processes tend to aggregate small particles and dissolved substances into larger particles that provide a substrate for heterotrophs and also make the particles more available to the animal population. The latter excretes soluble organics that help to maintain the food web. These complicated relations between the ocean creatures and the nonliving organic components are the subject of this paper.

Nonliving organic matter includes particles and masses of material of microscopic and even macroscopic size, small filter-passing particles and colloids, and material in true solution. The amount, in terms of organic carbon content, is of the order of 1 mg C/liter. Of this, one-tenth or less consists of particles large enough to be retained by filters with a pore size of 0.45 to 1.2 μ, such as are commonly used for separation. More than half the total will go through a Diaflo membrane that passes substances with a molecular weight of 50,000 or less.

Carbon measurements commonly involve destruction of the organic matter by wet or dry oxidation or by strong ultraviolet (UV) radiation, followed by measurement of the CO_2 evolved. There have been technical difficulties in development of the methods, and results obtained by different methods are not precisely comparable. However, these difficulties are minor compared with the problem of biochemical characterization of the material, which is chemically complex and too low in concentration, compared with the great mass of associated sea salts, for easy analysis. Only in the last few years have analytical techniques become sufficiently sophisticated and sensitive to deal effectively with this kind of problem, and the available information is still fragmentary.

Although the concentration of nonliving organic matter is small, the total amount in the world's oceans is large. A water column 1 m square extending from the sea surface to a deep ocean bottom of average depth, i.e., about 4000 m, would contain about 4 kg C/m^2, and the amount in all the world oceans would be 10^{12} metric tons or more. This is far in excess of the quantity of living organisms in the ocean, the ratio probably being of the order of 100 : 1.

The nonliving organic matter is derived from living organisms in the sea except for a small and probably insignificant amount from terrestrial sources, and the ultimate source is, of course, photosynthetic fixation of carbon in the surface layer. Opinions differ as to what might be a reasonable estimate of average oceanic productivity, but it almost certainly falls somewhere within the general range of 50 to 200 g C m^{-2} year^{-1}. Most of this production is metabolized within the food chain. Thus the large pool of nonliving matter must be the result of a slow rate of addition over a period of many years, and it follows logically that most of this material must be relatively inert biologically. However, a small fraction of the dissolved matter consists of amino acids and other simple organic compounds. Such substances are known to be excreted by animals and released as extracellular metabolites by algae, and in turn they are readily utilized by bacteria. This suggests that a small percentage of the dissolved matter may have a much more rapid turnover time than the general average. In this respect, and in other ways that will be discussed later, the interrelations between the living organisms of the sea and the nonliving matter are more complicated than was realized until recently.

DISTRIBUTION AND CHARACTER OF PARTICULATE ORGANIC MATTER

As indicated in the preceding paragraphs, there is a more or less continuous spectrum of sizes of organic matter. The particulate matter is operationally defined as the particles retained by a relatively fine filter, and this is a minor fraction of the total organic content. The method of collection obviously does not discriminate between living and nonliving matter, although subsidiary analyses of chlorophyll, ATP (adenosine triphosphate), or other components of living cells have sometimes been used for approximate estimates of living matter. The fraction of living matter in the surface layer is variable and sometimes large during periods of pronounced plankton growth. In the ocean depths it declines to 1 to 10% of the total.

Most of the available information on particulate organic matter is in terms of organic carbon. Scattered data can also be found on total dry weight, particle counts, a few other elements besides carbon, and some of the biochemical constituents. However, the preponderance of information on organic carbon makes it the most suitable analysis for discussion of regional and depth distribution.

Riley[1] in 1970 summarized the then-available data on the distribution of particulate organic carbon. Most of the values in the surface layer were in the range of 25 to 300 μg C/liter except in a thin surface stratum where the quantities were considerably larger. Below the surface layer there was a transition zone of decreasing concentration to a depth varying in different areas from 200 to 800 m, and below that there was no systematic decrease with depth. The mean concentration in deep water varied in different parts of the North Atlantic Ocean from 12 to 50 μg C/liter.

In this early work the water column was not sampled at closely spaced depth intervals. Later and more detailed work[2,3] has demonstrated significant variations in individual samples, even at closely spaced depth intervals. Thus there is considerable evidence of layering and microstructure, although the scale of these variations has not yet been determined accurately.

Similar layering in the Pacific Ocean has been described.[4,5] Nakajima[5] had an extensive series of stations in the North Pacific, most of which showed a decrease from the surface to a minimum at the bottom of the mixed layer and a secondary maximum at mid-depths. In deep water there was no systematic decrease, as in the North Atlantic. However, there may be exceptions to this in areas where there is layering of major water masses. There are mid-depth and deep-water maxima in the South Pacific associated with intrusions of Antarctic Intermediate Water and Circumpolar Water.[6]

Compilation of data on regional distribution in the Atlantic Ocean[1] showed high values in rich upwelling areas off the west coast of Africa and moderately high ones in temperate and boreal waters. Minimal values were obtained in poorer areas of the subtropics and tropics. Thus there appeared to be a correlation between surface productivity and total particulate organic matter, and this was true of deep water as well as the surface layer.

This picture of geographical distribution was compiled from the results of various investigators, who used slightly different methods, so that one might question whether or not the data were sufficiently comparable to warrant quantitative regional comparison. However, more recently Nakajima[5] has obtained similar results in a broad regional survey of the North Pacific Ocean using methods that were comparable throughout. The fact that deep water as well as surface particulate matter is correlated with surface productivity is not fully understood, although several possible reasons can be given. Discussion of this problem is relegated to a later section.

Visually, the most obvious components of the nonliving particulate fraction are fluffy amorphous masses of brownish material. Seen in the free floating state, they are more or less spherical, with numerous internal spaces that harbor bacteria, small algae, and protozoa.[7] Histochemical staining shows that they are mainly carbohydrate, although protein stains sometimes show a slight positive reaction.[2] Probably they are mainly polysaccharides. Chemical analyses[8] indicate the presence of algal cell-wall materials and refractory storage products.

Thin and semitransparent flakes constitute another major fraction. These flakes are irregular in shape, and the median size of the longest dimension is of the order of 25 μ. They are not obviously organic in nature on casual inspection, but they stain heavily with both protein and carbohydrate stains. They are indistinguishable visually from particles produced experimentally by adsorption of organic matter on bubbles. Indeed, it was only after experimental demonstration of this phenomenon[9] that they were recognized as being part of the organic component and were included among particle counts in seawater samples.[10] They are found in both surface and deep water, suggesting that there might be other modes of origin in deep water, but if so, the mechanism remains obscure.

Finally, the collection on the filter includes large numbers of small particles that are stained readily by histochemical stains but are not otherwise easily characterized. They presumably include small detrital fragments and clay and mineral particles with an organic coating.

"DISSOLVED" ORGANIC MATTER

Again this is an operational definition. Filter-passing matter is often called dissolved organic matter, but it obviously includes colloids and small particles up to the retention size of the filter.

The method most commonly used for measurement of this fraction has been wet oxidation. After preliminary acidification and degassing to remove inorganic CO_2, the sample is sealed and incubated with a chemical oxidant, most commonly persulfate in recent years. This is followed by further degassing and measurement of CO_2 produced by oxidation of organic matter. The ease of this method has led to fairly extensive application, although not without some skepticism as to whether all the organic matter could be oxidized by this method.

Most of the measurements are of the order of 0.5 to 1 mg C/liter. The highest values are found in the surface layer. In deep water, concentrations are low and relatively uniform both vertically and horizontally. Extensive observations in the North Atlantic by Duursma[11] showed some slight evidence of a mid-depth minimum in the vicinity of the oxygen minimum layer. However, no evidence of this was found in the South Atlantic,[12] and, in general, none of the slight variations that have been noted would seem to be very consistent or significant.

Skopintsev[13] developed a method for determining organic carbon by evaporating a seawater sample to dryness and releasing CO_2 by dry combustion. His results were considerably higher than the general level obtained by wet combustion, although he did not compare the two methods with duplicate samples.

Williams[14] described a method for destruction of the organic matter by strong UV radiation and subsequent analysis of CO_2 evolution. Comparison with persulfate oxidations showed that the latter were about 90% of the values obtained by UV oxidation.

Currently, several methods are under development for dry combustion, involving evaporation or freeze drying of the sample or direct injection of a small sample of water into the combustion chamber. Sharp[15] has developed the latter to a point where it yields results of usable precision, although it is not an easy method to use. The main difficulty is that the water sample injected into the combustion chamber must be small, and CO_2 evolution is near the limit of sensitivity of present detectors. Nevertheless, his observations provide the best data available on intercomparison of methods.

In a fairly large series of analyses of North Atlantic water, the general range was 0.76 to 1.74 mg C/liter, with a mean of 1.2. The mean for shallow samples (0 to 100 m) was 1.36; in deeper water (100 to 5000 m) the mean was 1.11. In 48 shallow-water samples, Sharp's method gave values averaging 0.186 mg C/liter higher than measurements obtained by wet oxidation of aliquot samples. In 54 deep-water samples, the difference was 0.262 mg. This is about twice as large as the difference between UV destruction and wet oxidation,[14] suggesting that dry combustion is more effective than either of the other methods.

Sharp fractionated a series of samples by passing them through filters of various pore sizes. The largest pore size was 0.8 μ, so that the organic matter retained was the fraction ordinarily regarded as particulate organic matter. Additional fractionation was obtained with a fine filter of 0.025 μ and a Diaflo membrane with an exclusion factor of 50,000 molecular weight, roughly equivalent to 0.003 μ. Results are shown in Table 1.

Comparison of dry combustion and persulfate oxidation showed no significant differences in the fraction that passed through the Diaflo membrane. The main difference was in the intermediate fraction. The meaning and significance of these results are by no means clear.

Indeed, very little is known as yet about the character and composition of filter-passing materials. At one time it was supposed that they were largely humic matter, such as one finds in freshwater as well as terrestrial situations. However, wet oxidation methods[11] show that ratios of carbon to nitrogen were remarkably low, of the order of 4 : 1 or less on the average, as contrasted with ratios of 10 : 1 or more which are commonly found in humates. In the case of the particulate matter, 85% of the organic nitrogen is in the amino form,[8] but this may not be equally so in the dissolved fraction. Certainly free amino acids are a small fraction of the total.[16] Urea is present,[17] and there are suggestions that urea condensates might be important constituents. All this awaits further study. Most of the attention has been centered on analyses of particular substances that are potentially significant biologically. The list is fairly long,[18]

TABLE 1

MEAN PERCENTAGE OF TOTAL ORGANIC CARBON IN SEAWATER SAMPLES

Particle-size range, μ	Mean % total organic carbon In samples from depths of 0 to 100 m	Mean % total organic carbon In samples from depths of >100 m
>0.8	2.3	1.6
0.025 to 0.8	7.1	15.4
0.003 to 0.025	16.2	20.2
<0.003	74.4	62.8

and it includes amino acids, carbohydrates, lipids, organic acids, and vitamins, but these are present only in trace amounts. There is a much larger pool of materials that presumably are end products of metabolism and are virtually inert biologically, and the composition of this fraction remains essentially unknown.

DYNAMICS OF PRODUCTION AND CONSUMPTION OF ORGANIC MATTER

Primary Sources

The basic source of organic matter in the sea is, of course, photosynthetic fixation of carbon in the surface layer, with some slight additions from the land. This organic matter then passes through a herbivore–carnivore food web, which, in the open ocean consumes most of it, and most of the consumption is within the upper few hundred meters. Excretory products and organisms that die a natural death pass into a parallel system of scavengers consisting mainly of bacteria, which gradually, in the water column or on the bottom, decompose the organic material and return the mineral elements for recycling through the system.

The preceding paragraph states the traditional view of the matter, and in broad outlines that view is correct for the open ocean, although recent work has introduced qualifications. Moreover, it is apparent that in some shallow estuarine waters the scavenger food chain is dominant, and the fauna gets its primary sustenance from decomposers working on marsh grass and other terrigenous or semiterrigenous sources rather than phytoplankton. There is a whole series of intergradations between these and open-sea conditions.

The Role of Nonliving Organic Matter in the Food Web

Early considerations of the dynamics of the food web were almost solely concerned with the interrelations of major groups of organisms: phytoplankton, zooplankton, nekton, benthos, and bacteria. The nonliving fraction, generally denoted as detritus, received scant attention. Much of what was said about it was contradictory. For example, there was a common concept that the role of decomposers was to degrade organic remains into progressively smaller particles and eventually to dissolved organic matter and mineralized elements. However, the most obvious detrital remains were the amorphous masses of material referred to earlier, which could not by any stretch of the imagination be identified as decomposing organisms. Detrital remains they might be, and are, in the light of recent research, but there was no speculation as to the mode of aggregation of small remains into larger masses.

In general, this detritus tended to be regarded as of doubtful nutritional value, but, paradoxically, many investigators regarded the so-called "rain of detritus" as the chief nutritional supply for the sparse deep-sea fauna. Or perhaps they were thinking more in terms of sinking bodies of dead copepods and larger organisms, but few of these have been recovered in bathypelagic net tows.

In recent years, increasing attention has been given to the development of an accurate description of nonliving organic matter in the sea, its possible roles in the food web, and experimental studies that bear upon these matters. Detailed discussion of the latter is given in the appendix, but some salient features may be summarized briefly:

1. Dissolved organic matter is not solely produced by bacterial activity. It is also a product of extracellular liberation by algae[19] and zooplankton excretion.[20] These products include amino acids and other compounds of low molecular weight that probably can be recycled directly into the food web via heterotrophic uptake by small organisms and possibly by other pathways that will be discussed later.

2. Although the chief function of bacteria in the food web is the decomposition of organic remains and eventual conversion to inorganic matter, this is by no means a simple process. Bacteria also are capable of aggregating small particles and possibly dissolved materials into flocculent masses that more or less resemble naturally occurring aggregates. These masses can provide a microcosmic environment for other small organisms and possibly a food supplement for larger filter feeders.

3. Small particles and probably dissolved organic matter can be adsorbed on bubbles, producing flakes that are indistinguishable from those found in natural seawater. Ultraviolet irradiation also stimulates particle formation. These processes would be operative only in the immediate surface layer and may be responsible for the observed fact that particulate organic carbon is several times higher in surface film collections than in slightly deeper water.

In short, it now appears that the interactions between living and nonliving matter are more complicated than was formerly supposed and that a good many of the reactions are reversible.

Organic aggregates in seawater harbor an abundant population of bacteria, small algae that presumably are heterotrophic, at least in deep water, and protista.[7] Their sources of nutrition have not been well established. The possibilities include utilization of some parts of the aggregates, absorption of dissolved organics, or a slightly more complicated mechanism in which adsorptive accretion of the particulate fraction is balanced by browsing activities of the heterotrophs.

Pomeroy and Johannes[7] measured the respiratory requirements of this so-called ultraplankton and obtained fairly large values, possibly equalling that of the larger zooplankton. They estimated that total carbon utilization by surface and mid-depth ultraplankton was approximately equal to "uncorrected" ^{14}C values for phytoplankton production.

The last statement requires some explanation. The routine method for measuring ^{14}C uptake has been criticized[21] because of errors due to self-adsorption on filters. The International ^{14}C Laboratory at Charlottenlund Slot has recommended that earlier results be increased by a factor of 1.45. In addition, the ^{14}C measurements do not, of course, record photosynthetic products that are liberated from the cells in soluble form. The combination of these two factors might mean that primary productivity is 50 to 100% higher than is indicated by ordinary ^{14}C values and therefore could account for the needs of both ultraplankton and the larger zooplankton.

The food requirements of mid-depth and deep-sea organisms and the role of nonliving organic matter in the bathypelagic food web present some very difficult problems. The "rain of detritus" theory has been challenged,[22,23] and it has been pointed out that much of the mid-depth fauna is migratory and is capable of feeding on living organisms in the surface layer at night more effectively than at the daytime level at mid-depths, thus physically transferring food from the surface to deeper levels. Further, random vertical movements below this level, with feeding and predation and death also randomized, would lead to a net downward transfer of food via active predation and without, necessarily, the mediation of sinking detritus.

This theory goes to the opposite extreme, and the truth probably lies somewhere between. Although most deep-water animals are predatory, there are a good many copepods with foliaceous appendages suitable for a filter feeding habit, although they might be feeding selectively as well. The guts of various deep-sea animals have been examined,[24,25] and there is no doubt that they feed on small heterotrophs. The copepods presumably are feeding on organic aggregates with their microcosmic assemblages, for they could not filter individual organisms of such small size with any degree of efficiency. However, this would not necessarily be so in the case of pelagic tunicates discussed by Fournier.[24] Harding[25] examined the gut contents of bathypelagic copepods and found flakes and other nonliving components as well as small heterotrophs. Histochemical staining procedures demonstrated a decrease in the protein content of flakes between the foregut and hindgut but little change in carbohydrate, suggesting partial utilization of this material. Earlier, Gordon[2] had treated collections of deep-water particulate matter with a mixture of trypsin, chymotrypsin, and amylase and had found that about 20% of the organic matter was hydrolyzed.

Riley[1] attempted to assess the feeding capabilities and food requirements of deep-water bathypelagic fauna by analogy with experimental information on cold-water surface populations, and he assumed, on the basis of Gordon's work, that about 20% of observed average concentrations of particulate matter could be utilized. The conclusion was that this kind of material could only be a food supplement, supplying at most about 20% of food requirements. However, these crude assumptions sweep some very large questions under the rug. We know essentially nothing about feeding capabilities or food requirements of deep-water organisms, so that the analogy with surface forms may or may not be valid. We also know nothing about their digestive capabilities, so that in vitro experiments with digestive enzymes may not give a realistic impression.

Selective feeding on larger particles or on organisms may make up for the apparent deficit. Or, as indicated earlier, there is considerable random variation in the quantity of particulate matter. The extent of this variation has not been carefully determined, but it is possible that the sparsity of deep-sea fauna may be controlled not so much by general impoverishment as by the improbability that any considerable number of animals will find the limited number of microhabitats that contain abundant food. All these possibilities that have been mentioned are ripe for further investigation.

Turning now to the bacteria and small algae in deep water, we note that experiments[26,27] have shown normal deep-water populations to be capable of absorbing ^{14}C-labeled sugars and amino acids at concentrations of 10^{-7} to $10^{-8}M$, and apparently this applies to algae as well as bacteria.[28] Rates of uptake varied for different kinds of substrate that were used, so that the results were not very meaningful ecologically, but, in general, they indicated that bacterial increase might be of the order of 10% per day. This is miniscule compared with optimal bacterial growth but is indicative that maintenance of a population is possible in deep water. This conclusion is reinforced by the fact that concentrations of free amino acids are one to two orders of magnitude larger than the minimum limits required for observable uptake.[16]

Finally we come to the point of trying to put the whole thing together. Not only in the surface layer but in the whole vertical column, there are regional variations in particulate matter in the North Atlantic[1] and the North Pacific[5] which appear to be related to geographical variations in surface production. The effect of surface production apparently is more important than horizontal dispersion in deep water, although a few cases have been noted in which there are vertical variations associated with particular water masses[6] or seasonal variations that probably are associated with water-mass transgressions.[1,29]

The high concentration of particulate matter underlying productive areas can hardly be explained in terms of passive sinking from the surface. Moderately large aggregates have a sinking rate of the order of 1 to 2 m/day and would require some years to reach bottom if they maintained their integrity throughout the descent.[1] Smaller particles would, of course, require longer. Of some significance in this respect is the report of McGill[30] that total organic phosphate varies regionally in relation to geographical variations in productivity. Most of this organic phosphate can be assigned to the filter-passing fraction rather than particulates, so that sinking is not directly implicated. However, the so-called dissolved organic carbon is more nearly uniform regionally and presumably represents an older fraction that has had more time to get uniformly dispersed.

An abundant literature could be cited in support of the conclusion that the whole biological system, surface to bottom, varies regionally more or less in accord with levels of surface productivity. Riley[31] reviewed some of this literature, chosen from a few selected areas. It was apparent there that the character of the food web can vary considerably from one area to another, with major emphasis on predators in some areas and on decomposers in others. Nevertheless, the generality holds and is that the surface production is in one way or another transported from surface to bottom, affecting the production of zooplankton, neckton and benthos, the quantity of small heterotrophic algae, nonliving particulate matter, and probably, to a limited degree, some of the filter-passing organic components. The reasons for this are not clearly understood, and explanations that can be presented are largely hypothetical.

The most important mechanism for vertical transfer is probably the so-called "ladder of life."[22,23] The nonliving organic matter and associated ultraplankton are eaten to some extent by bathypelagic copepods,[25] although, for the above-mentioned reasons, there is some question as to whether they are a major food item. Nor is there any solid information as to the degree of significance of animal excretion in promoting in situ formation of aggregates and the growth of small heterotrophs. The correlation between the size of the animal population and the amount of small particulate matter suggests this kind of reciprocal relation. Experimental information tends to support two postulates: (a) excretion of soluble substances could promote both the growth of heterotrophs and the accretion of nonliving aggregates, and (b) accompanying consumption of aggregates by the animal population would tend to stimulate further production of particulate matter. The latter might be enhanced by excretion of unconsolidated fecal material and of bacteria that are in a more active state of growth than those in the water column.

This general line of reasoning is supported by the observed fact that the amount of particulate organic matter does not decrease systematically with depth, which it might be expected to do if a significant amount were eaten or decomposed as it sinks through the water column. On the basis of this observation, it has been postulated[32] that a dynamic balance exists between consumption and accretion of particulate matter in the bathypelagic zone, although little was known then of the processes involved. Knowledge is still very inadequate, but the information that has accrued still supports the original postulate. There is as yet no way of estimating how much of the particulate matter in deep water represents residual material originating in shallow water and how much has been added by gradual accretion or has been formed *de novo* in deep water. However, the time scales that are involved would suggest that only the most inert materials could survive the long passage from surface to bottom.

Finally, estimates of the sedimentation rate of particulate matter on the deep ocean bottom are approximately equal to the estimated food requirements of the benthic fauna.[1] Most of this organic matter that settles out is utilized on the bottom, for the organic content of bottom sediments is far less than that of suspended particulates. This is not difficult to understand, for compaction of the settled material creates a relatively high concentration that should make it more vulnerable both to sediment feeders and to the kind of bacteria that are required to oxidize refractory organic substances with the mediation of dissolved organics that undoubtedly are more abundant in interstitial water than in the overlying water column. As sediment gradually accumulates on the bottom, the long, slow process of decomposition continues, so that the organic content declines with depth of burial until only a small fraction of the amount originally delivered to the sea floor remains permanently incarcerated.

APPENDIX

Experimental Information

Baylor, Sutcliffe, and Hirschfeld[9] and Sutcliffe, Baylor, and Menzel[33] reported that organic particles could be produced experimentally by passing a stream of bubbles through a column of filtered seawater. Riley[10] confirmed these results and reported that natural seawater contains flakes of particulate organic matter that are visually indistinguishable from the ones produced experimentally. This was part of a general study of the kinds and quantities of nonliving organic matter occurring in Long Island Sound. Subsequent papers[32,34] examined the distribution of organic matter in open waters of the Atlantic Ocean and reported further experiments on particle formation. The quantity obtained by bubbling surface seawater samples from impoverished areas, such as the Sargasso Sea, generally was less than the yield from rich inshore waters but was in turn significantly larger than the amount that could be produced from deep-ocean samples. There were suggestions in this early work that the largest quantities of nonliving organic matter and the greatest potential for experimental production were in places and times of major plankton growth and abundance. Large yields were also obtained by bubbling filtered media in which algal cultures had been grown.[34] Results implied that freshly produced metabolic products can be converted to particles more efficiently than in the case of the older dissolved matter ordinarily present.

Menzel[35] examined the process of particle formation with some improvements and modifications of earlier methods: (a) he found that his laboratory air supply was contaminated and developed a method for precombusting the air; (b) on second and subsequent filtrations, there was additional accumulation of carbon on filters, and he filtered his samples three times before bubbling; (c) he replicated samples and compared them with unbubbled controls. Under the conditions of his experiments, there was no significant particle formation.

Batoosingh, Riley, and Keshwar[36] reexamined the problem, comparing methods used by previous investigators. Large and significant yields were obtained after filtration through coarse filters; little or none was obtained after filtration through fine filters (0.2 μ) or triple filtration as practiced by Menzel. Thus it would appear that filter-passing particles are important as nuclei for the aggregation process, although the flakes that are formed are smooth and rather featureless and appear to be more than a mere condensation of particles.

Initial formation is rapid, but it approaches an asymptote after a day or so of continuous bubbling, and the maximum concentration attained is more or less similar to the original amount of naturally occurring organic carbon in the sample.

However, some of the experimental methods[33,36] have involved removal of particles during the bubbling period, and in such cases the total yield has greatly exceeded the amount that can be accumulated in suspension during ordinary experimental bubbling. This accumulation appears to inhibit further formation unless part of the yield is removed, but the mechanism for achieving this steady-state situation remains an enigma.

As indicated earlier, there is experimental evidence of particle formation mediated by UV light. This is thesis work in preparation by John R. Wheeler, and results are incomplete, but he has added lipids and amino acids to artificial seawater, and, after irradiation at approximately the intensity of UV in natural sunlight, there was chemical evidence of an increase in molecular weight, and microscopically visible particles were recovered. These appeared to be aggregates of smaller particles rather than flakes of the kind produced by bubbling.

These two processes obviously are limited to surface and near-surface waters. There is evidence of a third process that theoretically can take place anywhere in the water column. Sheldon, Evelyn, and Parsons[37] reported that small particles form spontaneously in filtered seawater, gradually shifting toward a maximum concentration with a particle size of about 4 μ at the end of 5 days. Refiltration was followed by further particle formation, and this cycle could be repeated several times. These investigators apparently thought that an equilibrium concentration was reached at the end of 5 days, with a carbon value that could be roughly estimated as about 25 μg/liter, although the actual measurements were made with a Coulter Counter.

Riley[1] examined this process over a longer period and found further increases that were largely associated with bacterial growth but were far in excess of any reasonable estimates of bacterial biomass. Filtration through millipore filters with a pore size of 0.45 μ, or even 0.2 μ, does not ordinarily sterilize the sample. There are small pleomorphic forms that pass through and subsequently develop into active growth stages of a larger size that can be measured visually or by plate counts. The bacteria go through a growth cycle in which the population increases to a maximum of the order of 30×10^3 cells/ml in the first 2 or 3 weeks and then declines to a smaller and relatively constant level of 10×10^3 or less. In other experiments in which a small quantity of a culture of *Pseudomonas* sp. was added to the filtered water, there was a similar growth cycle, except that the maximum and subsequent decline came more quickly.

Particulate organic carbon passed through a similar cycle. The maximum averaged 0.44 mg C/liter in a series of experiments with inshore Nova Scotia waters. The concentration in the later stable phase averaged 0.20 mg C. Visual examination suggested that living bacteria constituted only a small fraction of the total particulate matter. There were discrete particles and hazy, amorphous masses of material that more or less resembled naturally occurring organic aggregates except that they were more tenuous. Estimates of bacterial biomass based on plate counts and observed sizes indicated that living matter probably constituted 10%, more or less, of the total particulate carbon.

A few attempts were made to measure total carbon in the filter-passing fraction in order to get a complete carbon balance in the experiments. This was not altogether successful because the method was not precise enough for good results. However, the initial reduction in the filter-passing fraction was roughly twice the increase in particulate carbon, and subsequently there was no change within the limits of error of the method. This work needs to be repeated with better methods now available. However, the results can be interpreted to mean that (a) about half the initial decrease in the filter-passing fraction can be ascribed to utilization by bacteria and the other half to conversion of filter-passing materials to larger particulate matter; (b) the bacteria subsequently utilize some of the particulate matter and reduce it to a lower level; and (c) in the final stable phase, the remaining particulate matter is resistant to utilization (the fact that further reductions in the filter-passing fraction are too small to be detected by the methods used suggests that the bacteria are in a senescent condition).

The so-called stable phase was observed for periods of up to 4 months with only minor variations. However, in these experiments, as in the ones involving bubbling, removal of part of the particulate matter tended to induce further formation, so that a steady state was maintained with moderate cropping rates of the order of 7% per day. Larger rates of 20% per day could not be accommodated, and the quantity of particulate carbon gradually went down over a period of a month.

Attempts were made to determine whether bacteria were necessary for the aggregation process, and these were not entirely satisfactory because the drastic procedures necessary to eliminate bacteria may very well introduce artifacts.

Bacteria could be eliminated or reduced by at least two orders of magnitude (as indicated by plate tests) by triple filtration or treatment with dichromate or cyanide. In such cases there was no initial peak and only a slight increase in particulate carbon to an average level of 0.10 mg C/liter.

Discussion of Experiments

Bubbling experiments show that flakes can be formed which are indistinguishable from those found in nature, and surface wave action could provide a significant means of converting small particles and dissolved materials into larger particles that contain both protein and carbohydrate and could be a significant food item. Experimentally produced particles have been shown to support the growth of *Artemia*,[38] and evidence about utilization of naturally occurring particulate matter has been examined.

However, there is an enigma here, in that flakes are also found in deep ocean waters. They have a slow sinking rate and could hardly have been derived directly from the surface layer without consumption or dissolution in passage. Possibly there is an as yet unknown mode of formation, or possibly additional adsorption from the filter-passing fraction maintains their integrity.

As for the experiments on bacterial aggregation, the initial cycle of bacterial growth is regarded as an artifact of enclosure in experimental bottles, but the later steady state closely corresponds with conditions in nature. One of the big surprises in early investigation of the distribution of particulate organic carbon was that it did not decrease markedly from mid-depths on down. One would expect it to decline gradually with depth because of gradual consumption, but the kind of dynamic balance observed in experiments, which tends to maintain a sensibly constant concentration despite some cropping, would help to rationalize this distribution.

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DISCUSSION BY ATTENDEES

Olson: For a solar angle of 90° the UV cutoff is about 325 nm at the surface; and for a solar angle of 30°, the cutoff is about 350 nm. When you talk about the effect of UV on the formation of particulate organic matter, do you mean the wavelength region between 400 and 325 nm, and would not it be better to call this region near UV?

Riley: Those are the wavelengths that were involved. These were experiments in which the water was irradiated with approximately the intensity of natural UV in sunlight. There was formation of particles that could later be observed under the microscope, and there was incorporation of labeled amino acids and sugars. So it is a valid procedure at least experimentally, but it is very hard to say how important it is in the sea.

Holt: Sedimentation rates seem to be running averages due to the churning of sediments by bottom feeders. Would you care to speculate on the depth to which the sediments are indeed plowed?

Riley: It is true that some burrowing organisms can be found as deep as 10 or 20 cm below the surface, and there is constant reworking of the upper sediment layers. Considering the long time scale involved in sedimentation rates, this greatly smooths the curve for geological history.

Baylor: I address my question to you and to Dr. Cooke: What do you think of the suggestion that a calcium carbonate crystal of some kind, whether it came from an animal or whether it precipitated normally, would adsorb organic material from the seawater and then slowly sink until it was at a level that would dissolve it, thereby getting rid of the calcium carbonate crystal and leaving the adsorbed organic material? What do you think of this as a means of de novo formation of organic particles in the deep ocean?

Riley: Well, it would be ideal. It is a possibility. We have a real problem here in that we do find flakes in the deep sea, and we know that they are readily decomposed by bacteria.

Cooke: Once a lipophilic surface is produced, further accretions of material can certainly occur on it. Calcium carbonate produced in surface waters may indeed have some scouring effect on some classes of organic material in the sea, taking it to the bottom. This does not prevent the calcium carbonate from being dissolved; it only retards or alters the kinetics of the dissolution.

CARBON IN ESTUARIES

G. M. WOODWELL, P. H. RICH, and C. A. S. HALL
Biology Department, Brookhaven National Laboratory, Upton, New York

ABSTRACT

A crude estimate of the area of the world's estuaries indicates a total area of about 1.7×10^6 km^2 of which 3.8×10^5 km^2 is marsh and 1.4×10^6 km^2 is open water. Despite the large amount of research on estuaries in recent decades, there is little basis for an evaluation of equations that define relationships between net primary production, gross production, and various segments of total respiration in estuaries. A survey of the literature suggests that net primary production of estuarine marshes ranges from low rates averaging 1000 g (dry organic matter)/year in high latitudes to as much as 5000 g in the tropics. An average middle-latitude net production for the shallow water of estuaries seems to be about 1500 g (dry organic matter)/year. World net production of estuaries by this estimate is probably about 3.1×10^9 metric tons of organic matter annually or 2% of the total for the biota. Large exchanges of fixed carbon occur between estuaries and other water bodies. Most of the exchange occurs as "dissolved" organic matter. Sedimentation may also account for large amounts of net production. Rates of sedimentation of organic matter are probably fixed by the rate of rise of water against the land. The standing crop and productivity of fish in estuaries exceed those for all other natural water bodies.

Estuaries are commonly considered by scientists and many laymen as among the most vital elements of the interacting series of ecosystems that is the biosphere. They are, we say, "highly productive" and "essential" to maintenance of important coastal and oceanic fisheries. But when asked for a definition of "estuary" or for a measure of their size as a segment of the biosphere or for an appraisal of their total metabolism or their role in the world carbon or sulfur cycles, we must equivocate. Biologists, strangely enough, have been slow to measure the biosphere.

What are estuaries? What are their functions in the carbon budget? And what is their future?

Definitions seem simple, including the dictionary definition: "a passage where the tide meets the river current. . .a firth." Most students of estuaries accept the mixing of freshwater and salt water as a principal criterion identifying an estuary, but few have gone as far as McHugh[1] in defining estuarine waters simply on the basis of salinity. Using the 33.5% isopleth of salinity, he showed that substantial segments of the coastal oceans would be estuarine (Fig. 1). This definition makes good sense if one wishes to emphasize the continuity of biotic, physical, and chemical functions from coastal wetlands into the oceans. Most definitions, however, are more restrictive. Certainly in considering the carbon budget of the world, the carbon budget of oceans is to be differentiated from that of enclosed coastal waters.

The most common use is with reference to the mouths of rivers upstream to the limits of tidewater, to the enclosures behind baymouth bars, and to brackish lagoons. We use "estuary" in this more restrictive sense, making no attempt to differentiate bays that are not fed by freshwater in which there may be an accumulation of salt by evaporation. We include also marshlands, which in middle latitudes may accrue to 20 to 30% of the total area of large estuaries. We include also mangroves and estuarine swamp forests of the lower latitudes. We do not include coral reefs.

AREA OF ESTUARIES

We know of no detailed tabulation of the estuaries of the world beyond the map prepared by McHugh. The area and composition of estuaries are available for the United States from two recent comprehensive studies, the National Estuary Inventory[2] and the National Estuarine Pollution Study.[3] Table 1 was compiled from the National Estuarine Pollution Study. In the absence of other data, we have used the data for the United States to make an estimate of the area of estuaries of the world. The estimate was made by applying to the coastlines of the world the ratio of the area of estuary to the oceanic coast determined for the coasts of North America. We recognize that the area of estuaries varies greatly from one region to another. The east and Gulf coasts of North America have much greater areas of estuaries than the west coast, Alaska, or Hawaii (Table 1). The mean ratios of estuarine area per oceanic coastline for the United States, however, are probably not greatly different from mean ratios for North America or for other continents. An attempt to match topography and precipitation made no change in estimates for other continents on the basis of the average ratios for the United States. Such major estuaries as Chesapeake Bay, the Baltic Sea, and the mouths of major rivers were treated separately. We have estimated that on a worldwide basis 20% of the area of estuaries is marsh. Results are summarized in Table 2.

The total area of estuaries of the world appears by this estimate to be about 1.75×10^6 km^2. Of this, about 1.4×10^6 km^2 is open water and about 3.8×10^5 km^2 is marsh or mangrove. It would be surprising if estimates derived in this way were accurate within ±50%.

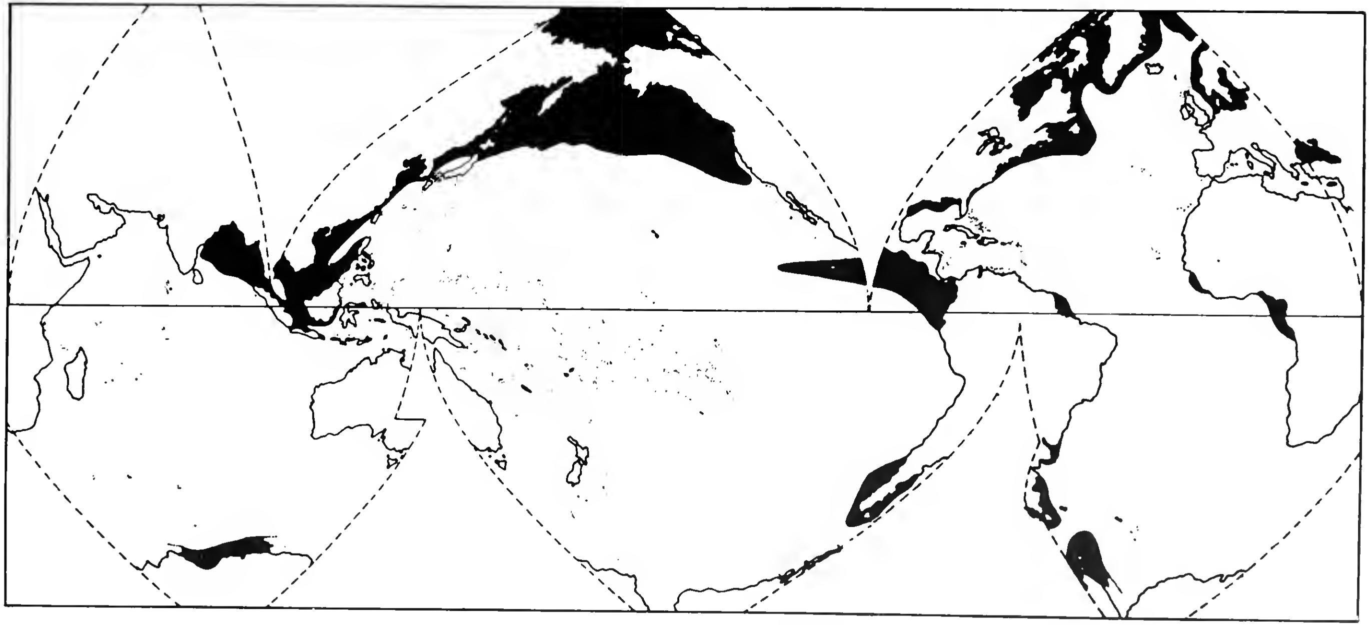

Fig. 1 Estuarine zones defined by the 33.5% isopleth of salinity. (From J. L. McHugh, *Estuaries*, p. 582, American Association for the Advancement of Science, Washington, 1967.)

TABLE 1

AREAS OF ESTUARY AND ESTUARINE MARSH IN THE UNITED STATES[*]

U. S. coastal zones	Coast, km	Estuary, km²			Ratios, km²/km		
		Water	Marsh	Water and marsh	Water/ coast	Marsh/ coast	Over-all
North Atlantic	2,186	8,866	253	9,059	4.03	0.12	
Middle Atlantic	2,070	13,287	1,562	14,849	6.41	0.75	
South Atlantic	1,315	10,290	5,872	16,162	7.82	4.46	
Florida	2,481	1,857	1,596	3,453	0.75	0.64	
Gulf of Mexico	3,652	28,335	21,826	50,161	7.76	5.97	
South Pacific	1,921	2,069	495	2,564	1.08	0.26	
North Pacific	1,076	5,040	115	5,155	4.68	0.11	
Alaska	23,972	37,174		37,174	1.55		
Hawaii	1,921	39	39	78	0.02	0.02	
Total	40,594	106,897	31,758	138,655	2.64	0.78	3.42
Chesapeake Bay		11,795	1,541	13,336			
Grand total		118,700	33,300	152,000			

[*] Source: National Estuarine Pollution Study, Report of the Secretary of the Interior to the U. S. Congress, March 1970.

THE FUNCTION OF ESTUARIES

Data in support of a comprehensive appraisal of the function of estuaries are also fragmented and incomplete. The most comprehensive studies of function have been made at Sapelo Island, Ga., and in the bays along the Texas coast.[4-10]

These and other studies, few in number, lead to the contemporary view that estuaries are highly "productive" of both fixed carbon and fish. The assumption has seemed reasonable that estuaries serve as centers of "outwelling" of nutrients and fixed carbon into the coastal ocean.[11] Their contribution to fisheries through spawning and nurture is widely recognized,[12,13] but data in support of their net role in the biospheric carbon cycle are limited.

One interpretation of the major routes of carbon movement in estuaries appears in Fig. 2, which was drawn specifically for Flax Pond, an estuarine marsh on the north shore of Long Island. Major exchanges occur here with Long Island Sound, with the uplands, with the sediments, and with the atmosphere, which are the four sides of the diagram. Within the estuary, there is net fixation of carbon by the Spartina marsh, by phytoplankton, benthic algae, and other plants. A major fraction of this fixed carbon enters detritus pathways in various forms, including "dissolved" and particulate organic matter (DOM, POM), and much of this ultimately participates in the complex oxidation–reduction exchanges of the sediments. But the possibility exists that the carbon flux of estuaries is dominated by large exchanges of fixed carbon with the land and with coastal waters. In Flax Pond the major exchange is with Long Island Sound.

The potential importance of large exchanges of fixed carbon between estuaries and other ecosystems nearby makes interpretation of the function of

TABLE 2

AREAS OF ESTUARY AND ESTUARINE MARSH*

World coastlines‡	Coast, km	Estuary, km² †		
		Water	Marsh	Total
United States	40,600	107,200	31,700	138,900
Canada	14,500	38,300	11,300	49,600
Mexico	23,500	62,100	18,300	80,400
South America	39,300	103,700	30,700	134,400
Africa	56,300	148,600	43,900	192,500
Europe§	42,300	111,700	33,000	144,700
Asia	76,400	201,700	59,600	261,300
Australia; New Zealand	34,600	91,300	27,000	118,300
Other¶	29,800	78,700	23,200	101,900
Total	357,300	943,300	278,700	1,222,000
Bays, deltas, seas				
United States (Chesapeake Bay)		11,800	1,500	13,300
Canada (St. Lawrence Gulf)		26,200	7,000	33,200
South America		41,400	11,000	52,400
Africa (Nile, Niger)		15,200	4,100	19,300
Europe (Baltic Sea)		305,600	76,400	382,000
Asia		19,800	5,000	24,800
Total		420,000	105,000	525,000
Grand Total		1,363,300	383,700	1,747,000

*Source map: *Man's Domain/A Thematic Atlas of the World,* 2nd ed., N. T. W. Thrower (Ed.), McGraw-Hill Book Company. Most coast measurements taken from Azimuth Equal Area Projections.

†Ratios are same as those applied to the United States in the National Estuarine Pollution Study. See Table 1.

‡Except where indicated, measurements do not include coastlines north of 60° N latitude.

§Includes Baltic sea coast, Norway west coast 60 to 70° N latitude, United Kingdom.

¶Crude coastline estimates of major portions of the Philippines, Indonesia, and Madagascar.

estuaries considerably more complex than that of lakes, rivers, or most terrestrial systems. One important tool in appraising the function of any unit of the earth's surface is net ecosystem production, the net change in the amount of carbon held by the system in a unit of time.[14] Interpretation and measurement of net ecosystem production for an estuary are especially awkward without clarification of the relationship between the fixed carbon participating in exchanges with

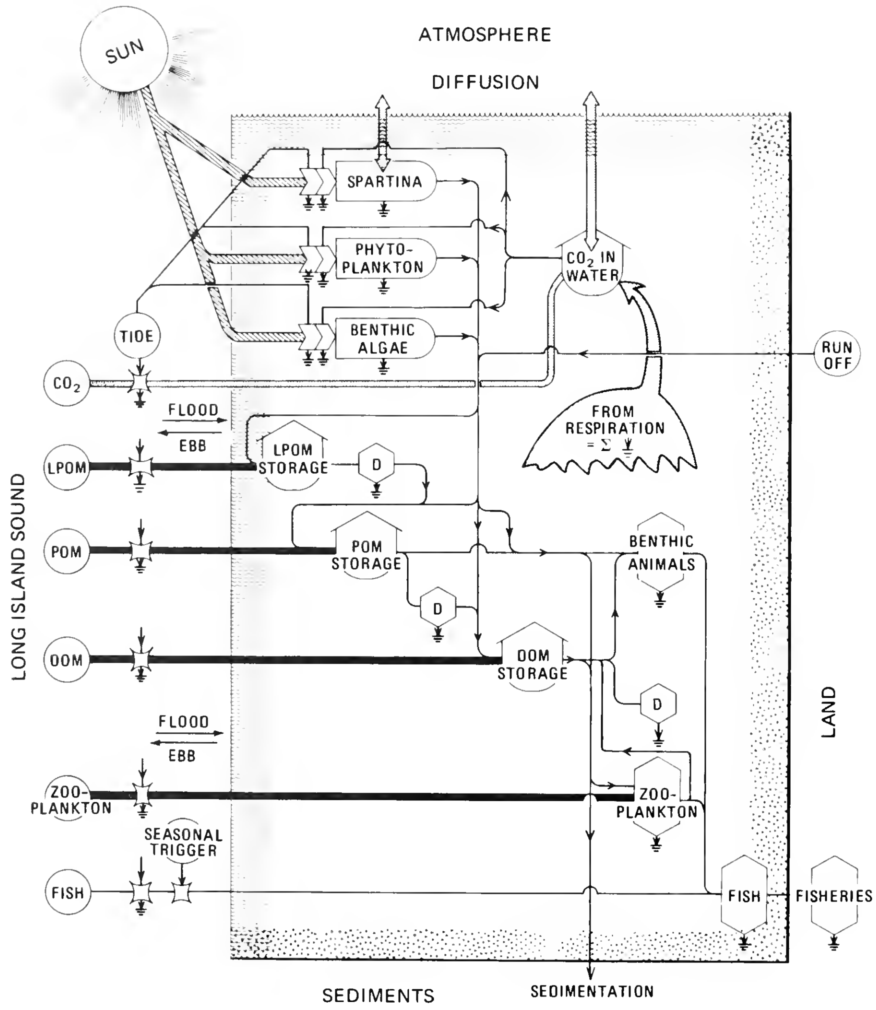

Fig. 2 Model of the carbon budget of Flax Pond, an estuarine marsh on the north shore of Long Island. Major exchanges occur between the marsh and Long Island Sound, the atmosphere, the sediments, and the uplands as indicated by the four sides of the diagram.

other systems to both the estuary's net production and net ecosystem production. Should that segment of net production of the estuary that is exported be considered part of net ecosystem production?

The earlier applications of net ecosystem production were to terrestrial ecosystems where exchanges with other systems were very small and could be ignored. In those instances, net ecosystem production was an expression of the net carbon balance of a unit of landscape. It was defined simply enough as the difference between gross production (GP) and total respiration (R_E):

$$NEP = GP - R_E \tag{1}$$

There appears to be advantage in extending the concept of net ecosystem production to apply to ecosystems where exchanges of fixed carbon with other systems are important by accounting for both inputs and losses. The original concept of net ecosystem production appears best preserved by the following modification of the equation:

$$\begin{aligned} NEP &= (GP + NP_I) - (R_E + NP_O) \\ &= \text{rate of accumulation or loss of carbon from} \\ &\quad \text{sediments or the biota} \end{aligned} \tag{2}$$

where NP_I is net production *in* and NP_O is net production *out*.

A principal objection to this formulation might be based on the possibility that NEP could be positive through import of fixed carbon into an area that had no gross production. We consider this a minor fault outweighed by the advantage that simple summing of NEPs for separate systems provides the NEP for the larger unit and ultimately for the biosphere as a whole.

The importance of exchanges in estuaries with uplands and with coastal oceans has been emphasized recently by recognition of the possibility that large amounts of fixed carbon may be transported as dissolved organic matter in water.[15] A daily net export of 1 mg C/liter in tidal water 1 m deep would be equivalent to 1200 to 1500 g (dry organic matter) m^{-2} $year^{-1}$ or the net production of many vegetations. This observation simply emphasizes the possibility that NEP for estuaries could be large and either positive or negative. The assumption seems questionable, however, that NEP drops to zero in estuaries at successional maturity as it seems to do in terrestrial systems. According to this analysis a positive NEP would indicate a net storage within the estuary, either as sediment or as increased biota; a negative NEP would indicate a net loss, which would appear as an input to some other system elsewhere. The possibility exists of course that, in estuaries where imports of fixed carbon may be large, total respiration is substantially higher than gross production. No clear indication of whether this is commonly or even rarely true is available at present. Data are, however, available on net production of estuaries and associated marshes, and limited inferences are possible.

A summary of data on the productivity of estuarine marshes is presented in Tables 3 to 6. Four different types of vegetation contribute to the productivity of estuaries: salt marshes and mangroves, submerged angiosperms, epiphytic and benthic algae, and phytoplankton. In each instance the number of separate estimates is small. The estimates of net production are difficult to compare, one with another and with studies of terrestrial ecosystems, because of differences in

TABLE 3

BIOMASS AND PRODUCTIVITY OF SALT MARSHES
(DATA FOR SHOOTS ONLY)

Region	Species	Biomass, g (dry weight)/m^2	Gross production	Respiration, g (dry weight) m^{-2} year^{-1}	Net production	Ref. No.
England	*Spartina townsendii*	700 to 1060	–	–	–	25, 26
Long Island	*Phragmites communis*	–	–	–	2695	27
	Spartina patens	–	–	–	993	27
	S. alterniflora (tall)	825	–	–	825	28
	S. alterniflora (short)	509	–	–	509	28
	S. patens	502	–	–	502	28
	Distichlis spicata	645	–	–	645	28
New Jersey	*Spartina alterniflora*	300	–	–	–	29
Delaware	*S. alterniflora*	413	–	–	445	30
Virginia	*S. alterniflora*	1332	–	–	–	31
	S. patens	805	–	–	–	31
	S. cynosuroides	1456	–	–	–	31
	Distichlis spicata	360	–	–	–	31
	Frimbristylis	605	–	–	–	31
	Borrichia	785	–	–	–	31
	Juncus roemerianus	650	–	–	–	31
North Carolina	*Spartina alterniflora*	545	–	–	650	32
	S. alterniflora (tall)	2100	–	–	1300	33
	S. alterniflora (tall)	1320	–	–	1296	34
	S. alterniflora (short)	259	–	–	329	34
	S. alterniflora (short)	250	–	–	610	35
	S. patens	640	–	–	1296	36
	Juncus roemerianus	1173	–	–	796	34
	J. roemerianus	–	–	–	560	37
	J. roemerianus	786	–	–	1360	36
	J. roemerianus	340	–	–	850	38
Georgia	*Spartina alterniflora*	–	–	–	973	39
	S. alterniflora	2248	8452	6844	1608	40
	S. alterniflora	–	–	–	3300*	41
Louisiana	*S. alterniflora* (tall)	925	–	2800	–	42
	S. alterniflora (short)	600	–	1950	–	42
Florida	*Juncus roemerianus*	232	–	849	–	43
Puerto Rico	*Rhizophora mangle*	11285*	–	–	–	44

*Includes roots.

TABLE 4

BIOMASS AND PRODUCTIVITY OF SUBMERGED ANGIOSPERMS

Region	Species	Biomass, g (dry weight)/m^2	Gross production	Respiration, g (dry weight) m^{-2} year^{-1}	Net production	Ref. No.
Rhode Island	*Zostera marina*	66*	–	–	–	45
Long Island	*Z. marina*	2464	–	–	–	28
Florida	*Thalassia testudinum*	3300	4000	1800	2200	46
Puerto Rico	*T. testudinum*	5660	–	–	4000	47

*Aboveground portion only.

TABLE 5

BIOMASS AND PRODUCTIVITY OF EPIPHYTIC AND BENTHIC ALGAE

Region	Species	Biomass, g (dry weight)/m^2	Gross production	Respiration, g (dry weight) m^{-2} year^{-1}	Net production	Ref. No.
Long Island	*Ulva lactuca*	785			785	28
Georgia	Microscopic benthic algae	–	440	–	400	48
Louisiana	Benthic algae	–	712	–	370	42
	Epiphytic algae	–	–	–	143	42
	Epiphytic algae	–	–	–	71	42
Florida	Epiphytic algae	–	1075	575	500	46

methods of measurement. Although we would like to contribute directly to an evaluation of Eq. 2 for the world's estuaries by appraising both net and gross production, the difficulties of measurement restrict us to a focus on net production that occurs within estuaries. Where there are no exchanges of net primary production with other ecosystems, net ecosystem production equals net primary production minus the respiration of heterotrophs.

Wetlands

In Table 3 we have summarized 20 reports of measurements of production in estuarine marshes and mangrove communities. The figures for net production are for shoots only, except as indicated. There are no separately identifiable data on root production in these vegetations. The assumption that root production is equivalent to shoot production gives a range of net productivities from about 1000 to 3500 g (dry organic matter) m^{-2} year^{-1}

TABLE 6

BIOMASS AND PRODUCTIVITY OF PHYTOPLANKTON*

Region	Locality	Biomass, g (dry weight)/m^2	Gross production	Respiration, g (dry weight) m^{-2} year^{-1}	Net production	Ref. No.
Denmark	Isefjord	–	–	–	650 to 1075	49
Nova Scotia	–	–	–	–	475	50
British Columbia	–	–	1625	–	1125	51
Washington	Columbia River	–	–	–	–	52
	Upwelling north of river	–	–	–	380	–
	River mouth	–	–	–	220	–
	Ocean beyond river	–	–	–	152	–
	River plume	–	–	–	150	–
New York	Long Island Sound	–	1175	–	512	53
	Hempstead Bay	–	–	–	987	28
	Shallow water off New York	–	–	–	400	54
	Continental shelf	–	–	–	300	54
	Continental slope	–	–	–	250	54
North Carolina		–	249	–	131	55
Georgia	Coastal water	–	–	–	1368	56
Mississippi	Coastal water	–	–	–	720	57
Louisiana	Barataria Bay	–	898	–	425	42
India	Cochin backwater	0.5	702	–	310	58

*Values given in g C/m^2 were multiplied by 2.5 for g (dry weight)/m^2.

Submerged Angiosperms

Four reports of net production of submerged angiosperms suggest a range of 2200 to 4000 g m^{-2} year^{-1} (Table 4). All reports are from southern latitudes.

Epiphytic and Benthic Algae

Net production of attached algae can probably be measured with reasonable precision simply by harvest techniques, although there is always question as to losses through grazing and losses of soluble compounds. The data suggest a range of net production from 71 to 785 g (dry organic matter) m^{-2} year^{-1}. No latitudinal or other trend is conspicuous (Table 5).

Phytoplankton

The methods used in measurement of net production of phytoplankton also leave many questions as to precisely what has been measured and the magnitude of errors. The range of data in Table 6 is from 131 to 1368 g (dry organic matter) m^{-2} $year^{-1}$. No latitudinal trend is apparent, although a wide range of latitude is spanned.

Open Water

Net production in the open waters of estuaries of the world may average 1000 to 2000 g (dry organic matter) m^{-2} $year^{-1}$. Where phytoplankton production dominates, productivity is probably lower; where submerged angiosperms or large attached algae are abundant, production would seem to be higher, perhaps considerably higher.

These limited data support the assertion that estuaries are "productive" of net primary production. The wetlands or marshes are most productive, although not spectacularly more productive than cane fields, rich woodlands, freshwater marshes, or various communities of cultivated plants.[16-18]

Distribution of Net Production

In estuaries there may be substantial imports of fixed carbon from uplands, exchanges of carbon with coastal oceans, and exchanges with sediments. There is no report of these exchanges available currently, although there is obvious need for clarification of their magnitudes and function. Limited insight as to the importance of the exchanges is available from an appraisal of the C budget of a tidal salt pond on Long Island. Flax Pond is a 50-ha (hectare) marsh, open to Long Island Sound (Fig. 3). Freshwater inputs are limited; it is flushed twice daily by the tide. The study has been under way for about 1 year.

The flux of dissolved organic carbon (DOC) through the single channel connecting the marsh to Long Island Sound is potentially very large. Originally we had assumed that there would be a large net flux into the Sound. This appears questionable at present. Data compiled through the first 7 months of a 2-year sampling program show that between June and December there was a net flux of fixed carbon into the marsh from Long Island Sound (Fig. 4). The largest influx occurred during the summer and fall, especially September and October. During 3 months a total quantity of C equivalent to 800 to 1000 g (dry organic matter)/m^2 was retained in the estuary. This is equivalent to the net production of many vegetations. During winter and spring there appears to be a regular loss of dissolved organic carbon. The balance for the year will probably be approximately zero. The flux of particulate organic matter (POM) parallels that of dissolved organic matter. The total quantities of particulate are about 10% that of dissolved. The flux of large particulate matter (LPOM) in forms such as *Spartina* stems appears to be still smaller. In Flax Pond it is less than 1% of the POM.

Measurement of C as total CO_2 shows, as might be expected, a continuous efflux of C from the estuary into the Sound, the total efflux approximating the influx of DOC.

Fig. 3 Flax Pond, an estuarine marsh on the north shore of Long Island. The marsh is connected through a single channel to Long Island Sound.

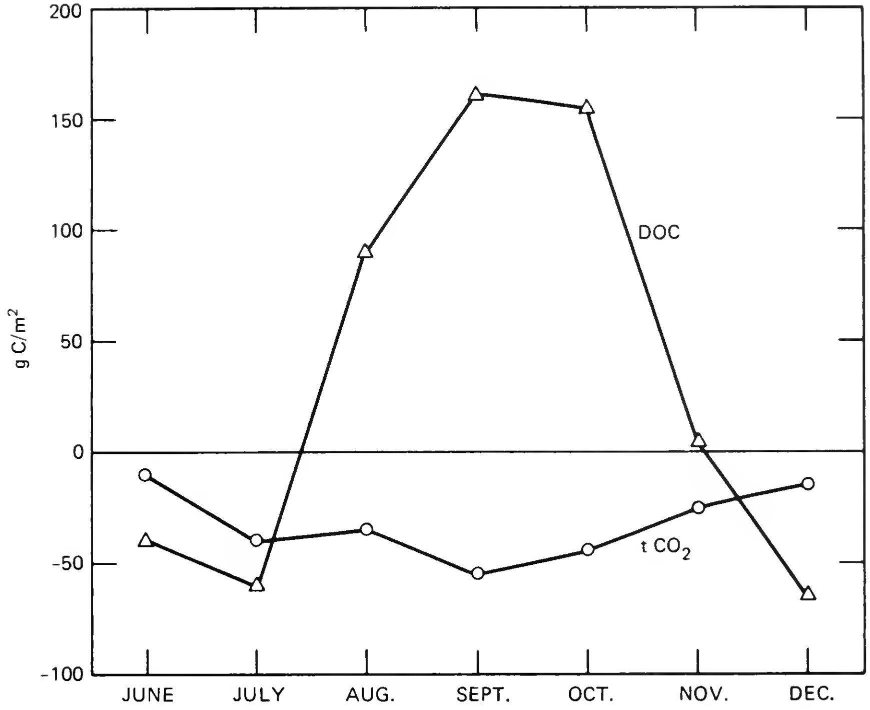

Fig. 4 The flux of dissolved organic carbon (DOC) and total CO_2 through the Flax Pond channel in 1971. Losses from Flax Pond are indicated below the zero line.

Sedimentation

Some fraction of the fixed carbon entering estuaries participates in exchanges with sediments, driving segments of such important mineral cycles as S and N, discussed elsewhere in this symposium.

Accumulations of fossil fuels, peat, and shallow organic sediments leave little question of the importance of sedimentation in removing carbon from circulation, at least temporarily. The rate of sedimentation is measurable in part. In the marsh at Barnstable, Mass., the rate of accumulation of peat was measured by Redfield and Rubin,[19] as indicated in Fig. 5. A change in the rate of rise of water against the land accounts for the shift in slope of the curve and emphasizes the importance of this factor in determining storage of C. In the modern world we have seen many examples of how rapidly eutrophication of estuaries and other shallow-water bodies can build substantial accumulations of organic sediments locally. Worldwide, however, it seems reasonable to assume that water-level fluctuations are more important in affecting the rate of accumulation of C in estuarine sediments than other factors. The maximum rate at which C can

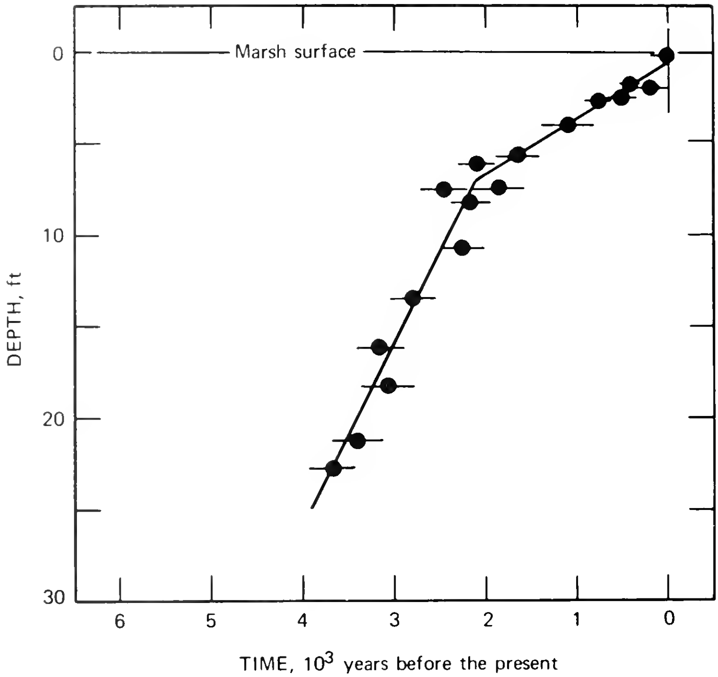

Fig. 5 Relationship between age and depth of high marsh peat at Barnstable, Mass. (Alfred C. Redfield, *Estuaries*, p. 113, American Association for the Advancement of Science, Washington, 1967.)

accumulate probably approximates the rate of net productivity. The import of fixed C from uplands and from the coastal ocean might increase the rate locally above the net production under extraordinary circumstances.

Fisheries

The fish populations of estuaries are higher than those of freshwater bodies and commonly higher (sometimes 1000 times) than in other coastal waters (Fig. 6). Standing crops in segments of Flax Pond occasionally exceed 100 g (dry weight)/m^2. Productivity of fish in estuaries often ranges from 5 to 15 g (dry weight) m^{-2} $year^{-1}$ and is probably the highest of any water bodies. (Dry weight of fish is approximately 20% of wet weight.) The total contribution of estuaries to oceanic fisheries has been documented.[12,20] Of the estimated 3×10^6 metric tons of fish and shellfish caught in western Atlantic continental shelf waters, about two-thirds are from species believed to be estuarine dependent at some stage in their life history. Stroud[21] calculated that each hectare of estuary contributes more than 550 kg fish each year to coastal fisheries, either directly or by serving as nursery grounds for the young of fish captured offshore. The

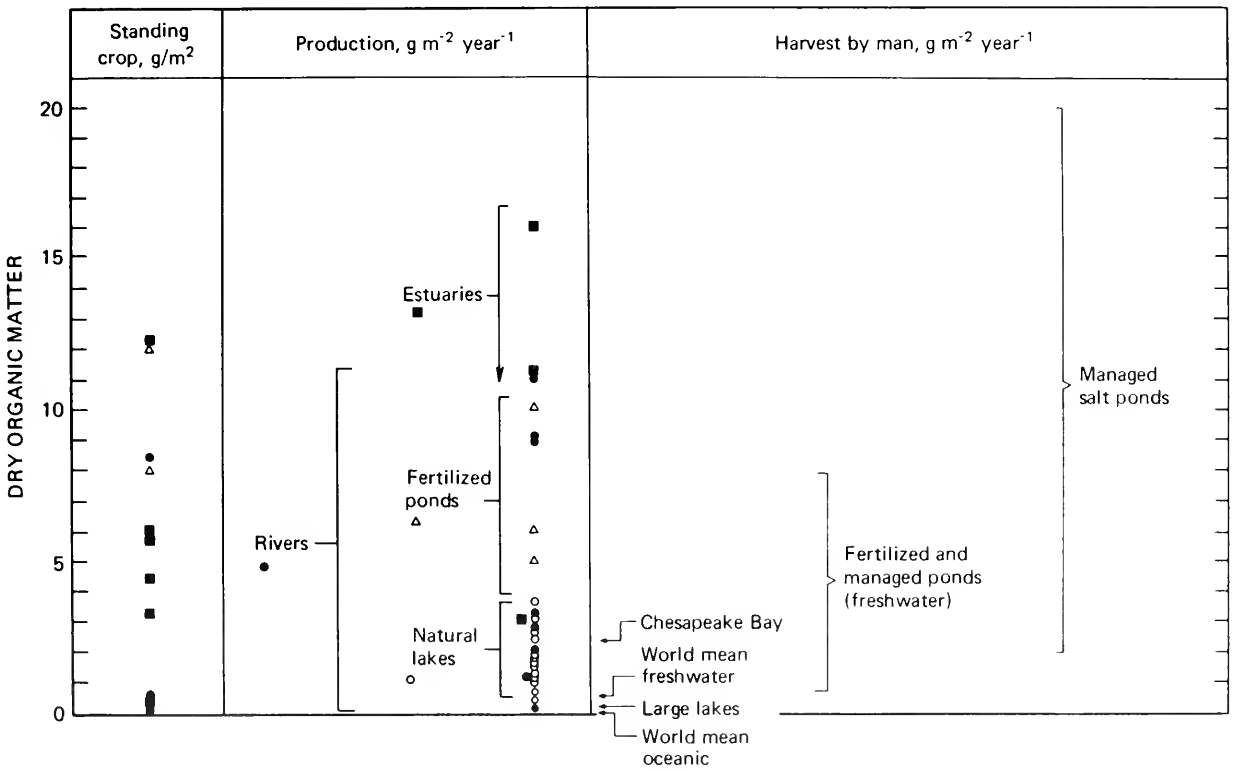

Fig. 6 Standing crop, production, and yield to man of various aquatic ecosystems. Live weight is approximately five times that of dry organic matter.[59-74]

protein yields from managed estuarine regions equal or exceed protein yields from managed terrestrial systems producing beef.[22]

THE CARBON BUDGET OF THE WORLD'S ESTUARIES

Experience with Flax Pond suggests that there is not a large steady efflux of fixed carbon from estuarine marshes into coastal waters. In such estuaries the flux may be the opposite with the marsh removing fixed carbon from tidal waters. Earlier experience seems to show that the dissolved organic matter of the oceans ($\sim$1 mg/l) does not originate in the Amazon[23] and probably does not originate in other estuaries.[15] If this relationship applies generally, and sediments are accumulating, net ecosystem production as we have defined it must be positive for the estuaries of the world. Estuaries appear to be centers of high primary production, high metabolism, and centers of sedimentation; they may not normally be centers of outwelling of fixed carbon into coastal oceans.

The magnitude of NEP in estuaries obviously depends on the division of the carbon flux between metabolism and sedimentation. The rate of sedimentation is controlled both by the rate of input of fixed carbon and the rise of sea level against the land. The input of fixed carbon (NEP) can be appraised but crudely at present. It is the net production of plants within the estuary (gross production less respiration of autotrophs) plus the balance between influx and efflux (Eq. 2). Net production can be estimated from the literature summarized above for marshes and open water.

The amount of primary production in marshes appears to vary with latitude. Assuming that the world's marshes are divided equally among those having net productions of 1000, 2500, and 5000 g (dry organic matter) m^{-2} $year^{-1}$, the annual net production of the world's marshes would be 1.09×10^{15} g (dry organic matter) (1.09×10^9 metric tons). If C is 0.45 of this dry matter, then there would be 4.9×10^8 metric tons C entering the world's marshes annually as net production.

Estuarine waters are less productive but larger in total area. Assuming that mean net production of estuarine waters is 1500 g (dry organic matter) m^{-2} $year^{-1}$, the world total is 2.04×10^9 metric tons (dry organic matter)/year, equivalent to 9.18×10^8 metric tons C. Total net production of the estuaries and estuarine marshes is thus 3.13×10^9 metric tons (dry organic matter)/year or 1.41×10^9 metric tons C. An earlier estimate by Whittaker and Likens (cited by Whittaker and Woodwell[24]) suggests that world estuaries might contribute 4×10^9 metric tons (dry organic matter) as net production to a world total net production of 164×10^9 metric tons. Thus, although estuaries as we have defined them include an area of approximately 0.25% of the earth's surface, their net production by this estimate is about 2% of the world net production.

Direct, short-term measurements of rates of sedimentation are difficult to make with accuracy. An appraisal of current data is beyond our scope, but such an appraisal is important to a clear resolution of the role of estuaries in the world carbon budget. Despite the possibility of a large influx of fixed carbon from outside estuaries, the NEP of estuaries probably does not exceed over large areas the mean net primary production of the estuary.

Total respiration is the most direct measure of biotic function and of the division of the carbon flux between metabolism and sedimentation. A limited number of partial appraisals confirm that metabolism is high.[6,8,40] The most convincing evidence, however, remains data from samplings of fish, which seem to confirm that a major segment of the net production goes to support living systems. Our review suggests that 0.1 to 1.0% of net production of estuaries may be harvestable as fish. This efficiency of transfer of net primary production to fish production is similar to the 0.25% estimated by Ricker[22] for the North Sea. Thus the higher productivity of fish in estuaries seems to be due not to higher efficiency of energy transfer to fish but to higher primary production.

CONCLUSION

The simpler aspects of the morphology and hydrodynamics of the world's estuaries have been described in detail in other works; this review shows that what we know of the broadest biotic functions of estuaries is still largely guesswork. Simple questions are still useful; What do estuaries do as units of the biosphere? The most broadly useful answers would come through an evaluation of the production equations for the world's estuaries, including an appraisal of inputs, outputs, rates of sedimentation, net production, and total respiration. These data are currently being acquired and should, with new data on the area of estuaries available through satellite mapping, bring major improvements in the precision of analyses, such as this one.

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DISCUSSION BY ATTENDEES

Riley: Does groundwater seepage contribute a significant amount of dissolved organic carbon (DOC) to Flax Pond?

Woodwell: I do not know. Some of the groundwater of Long Island certainly contains organic compounds. I do not know whether significant horizontal movement of these compounds occurs.

Likens: DOC averages about 1 mg/liter in groundwater at the Hubbard Brook Experimental Forest in New Hampshire.

Woodwell: Dr. Wetzel points out that in a lake in which he and his colleagues have worked, about one-third of the DOC comes in as dissolved carbon in groundwater.

Dr. Charles Hall points out that in Flax Pond, the estuary that I spoke of, the groundwater probably does not carry a large fraction of the DOC into the pond because the flux of water and DOC through tidal exchanges with Long Island Sound is very large.

Dr. Allen asks if we have any measurements of atmospheric exchanges of carbon in Flax Pond. The answer is that we do not; we plan to do an intensive study of just those exchanges a year from now.

Olson: How are we supposed to compare length of coastline with areas of estuary in Fig. 1?

Woodwell: The National Estuarine Pollution Study includes a tabulation of the area of estuary for diverse sections of coastline of the United States, including Alaska and Hawaii, and provides those ratios. The ratios are in the range of about 0.03 to about 9 sq miles of estuary including marsh per mile of coast. We applied the average for all coastlines to the temperate- and tropical-zone coastlines of the world. We measured the coastline lengths ourselves on maps of uniform scale. We considered large estuaries separately—river mouths, Chesapeake Bay, the Baltic Sea. This is a very crude way of obtaining the data, but there appears to be no other tabulation.

CARBON IN FRESHWATER SYSTEMS

ROBERT G. WETZEL* and PETER H. RICH†
*W. K. Kellogg Biological Station, Michigan State University, Hickory Corners, Michigan;
†Biology Department, Brookhaven National Laboratory, Upton, New York

ABSTRACT

Among the great diversity of concentrations and states of inorganic carbon of freshwaters, a number of situations exist where free CO_2 in equilibrium with the atmosphere may be inadequate for metabolism, or indirectly inadequate as a result of chemical losses from the system. Serious limitations to photosynthesis by inorganic carbon per se are unlikely, although shifts to assimilation of bicarbonate at metabolic expense are common.

The origins, rates of production, and fates of detrital dissolved and particulate organic carbon of a small temperate-zone lake are summarized to exemplify the importance of detrital–dynamic aspects of freshwater systems. The concept of net ecosystem productivity is reviewed and applied to the example. Major contributions by the littoral producers and from allochthonous sources are demonstrated and discussed in relation to increasing fertility. Within this spectrum of autochthonous and allochthonous inputs of organic carbon, the relative contribution by differing modes of metabolism to dissolved and particulate carbon pools is considered.

A majority of the carbon present in freshwater systems occurs as equilibrium products of carbonic acid. A smaller amount of carbon occurs in organic compounds as dissolved and particulate detrital carbon, and a small fraction occurs as carbon of living biota. The complex equilibrium reactions of inorganic carbon and the distribution of species of total CO_2 ($\Sigma CO_2 = CO_2 + HCO_3^- + CO_3^{2-}$) are understood in considerable detail. Similarly, rather sophisticated knowledge of the structure and function of lacustrine and lotic biota is available. Much less well understood are the structure and functional interrelationships of the large fraction of dissolved and dead particulate detrital carbon in aquatic ecosystems. Separation of inorganic, detrital organic, and biotic carbon is arbitrary, though essential for analytical purposes. True insight into causality and control necessitates an understanding of their functional relationships.

INORGANIC CARBON

In most freshwaters, inorganic carbon dominates over organic forms and exists almost totally as equilibrium products of CO_2 and carbonic acid. The quantitative diversity of inorganic carbon (ΣCO_2) of lakes is extreme. Inland waters range from solutions chemically similar to distilled water to highly saline carbonate brines in which ΣCO_2 exceeds several moles per liter. A more typical range for ΣCO_2 is 50 micromoles to 10 millimoles, the latter not uncommon in hard-water lakes of glaciated morainal regions of the temperate zone.

Dissociation equilibria and kinetics of the hydration and dehydration of CO_2 are very well delineated in pure-solution chemistry [e.g., see extensive reviews of Kern (1960), Raven (1970), and Stumm and Morgan (1970)]. Free CO_2, HCO_3, or pH can be computed from activity theory if two variables and the pK are known, yielding concentration (or activity of CO_2 as H_2CO_3) in solution rather than analytical free CO_2 (Hutchinson, 1957). Practically all determinations of $[\Sigma CO_2]$ are made from empirical measurements of pH and $[HCO_3^-]$. Although calculated and analytical CO_2 are identical at pH 7.6, large discrepancies occur when calculated ΣCO_2 is compared to analytically determined CO_2 over a spectrum of pH values (Hutchinson, 1957; Wood, 1970). At pH >8, calculated values greatly exceed analytical values; at low pH, calculated ΣCO_2 is larger than analytical CO_2, in part a result of interferences by organic acids.

Atmospheric CO_2 (about 0.033 vol.%) dissolves in water to yield an unhydrated CO_2 concentration similar to that in air (about 10 micromoles). The hydration of CO_2 to H_2CO_3 is relatively slow chemically (e.g., 15 sec), which results, at equilibrium, in a concentration of H_2CO_3 0.0025 times that of CO_2. The dissociation of H_2CO_3 to HCO_3^- and CO_3^{2-} is essentially instantaneous. If CO_2 is in equilibrium in a solution buffered to constant pH, the $[CO_2]$ and $[H_2CO_3]$ are independent of pH, whereas $[HCO_3^-]$ and $[CO_3^{2-}]$ increase with pH until saturation kinetics are achieved. These equilibria are strongly modified by temperature and salinity. At the salinity of seawater, pK_1 (HCO_3) is about 0.5 unit, and the pK_2 (CO_3^{2-}) about 1 unit, lower than freshwater (Raven, 1970). Both oceanic and freshwaters are close to equilibrium with atmospheric CO_2. In the marine habitat the inorganic-carbon pool contains about 2 millimoles C, largely as HCO_3^-, a reservoir some 50 times that of the atmosphere. In freshwaters, ΣCO_2 is much more pH dependent in relation to $[HCO_3^-]$ and $[CO_3^{2-}]$.

In marine systems, inorganic-carbon fluxes are, for all practical purposes, associated with these inorganic ionization equilibria. In freshwaters, biotic respiratory sources and fluxes of CO_2 can be significant to overall carbon metabolism. We will return to this point later.

The diffusion of CO_2 from the atmosphere and the dissociation kinetics of dissolved carbonates are obviously of major importance to photosynthetic organisms dependent on inorganic-carbon availability. The magnitude of CO_2 exchange between the atmosphere and water cannot be determined by partial-pressure differences alone. Many lakes near neutrality are slightly supersaturated with CO_2 relative to the atmospheric pressure of CO_2. Many other waters are not in equilibrium with the CO_2 of the atmosphere (although they may be with other gases, e.g., oxygen) because of low turbulence and slowness of gas-transfer reactions, especially in alkaline bicarbonate waters containing carbonate in large amounts. Diffusion of atmospheric CO_2 has been elaborated by Broecker and coworkers (1965, 1968, 1971, 1972) where techniques of determining gas transfer between the atmosphere and water have been measured by ^{226}Ra decay and flux of ^{222}Rn. Where applied to a soft-water lake of the Canadian Shield of very low ΣCO_2, atmospheric invasion of CO_2 was adequate (0.12 ± 0.06 g C m^{-2} day^{-1}) to account for 30 to 90% of the carbon fixation by phytoplankton (Schindler et al., 1972). How universal such diffusion rates are, how they shift seasonally during ice-free periods, and how they are affected within an array of dynamic chemical and biotic CO_2 demands on, and fluxes by, the system remain obscure.

In addition to highly dynamic biotic demands for CO_2 and inputs of CO_2 to freshwaters, complex shifts in precipitation and dissolution reactions of carbonate occur spatially and temporally. In alkaline hard-water lakes, much larger (2X) concentrations of calcium and bicarbonate are commonly found than would be expected on the basis of equilibrium with pressures normally found in the atmosphere (Ohle, 1952; Wetzel, 1966, 1971). The solubility product of $CaCO_3$ is low (0.48×10^{-8}), and $CaCO_3$ can start precipitating from calcareous waters when the pH is sufficiently high (uniformly in a buffered system or in microzones associated with active photosynthesis). However, very large amounts of inorganic carbon may exist as carbonate and $CaCO_3$ in metastable conditions, and there is strong evidence that considerable $CaCO_3$ occurs in a stable colloidal form. The importance of colloidal $CaCO_3$, in addition to larger particulate $CaCO_3$, is just beginning to be appreciated in relation to indirect effects upon metabolism and flux rates of organic carbon.

Labile organic compounds (amino acids, fatty acids) adsorb strongly to particulate and colloidal $CaCO_3$ (Chave, 1965; Chave and Suess, 1970; Suess, 1968, 1970; Meyers and Quinn, 1971a; Wetzel and Allen, 1972). Although such adsorption could be viewed as scavenging and concentrating labile dissolved organic carbon from dilute solution for a more ready utilization by bacteria, empirical evidence indicates, rather, a chemical competition with the bacteria for the substrates. A large fraction of $CaCO_3$ is precipitated during photosynthetic removal of CO_2 by algae and macrophytic vegetation. Frequently the plant cells serve as a nucleus for particulate-$CaCO_3$ formation, which occurs at the site of simultaneous secretion of organic compounds. This association of dissolved organic detrital carbon with $CaCO_3$ is a component of certain freshwater systems which affects the chemical milieu without clearly defined energetic transformations (Wetzel, Rich, Miller, and Allen, 1972). The organic coatings also inhibit dissolution of sedimenting $CaCO_3$ in lakes and form a major sink for inorganic and organic detrital carbon (Wetzel, 1970, 1971).

It is evident that estimates of theoretical dissociation constants and kinetics of the ΣCO_2 complex derived from pure solutions differ significantly from in situ results in natural waters. However, in most freshwater systems, dissociation rates of ionic CO_2 species and the maintenance of near-equilibrium conditions between atmospheric CO_2 and the water are sufficiently rapid that severe inorganic-carbon limitation to photosynthesis is unlikely, even under conditions of low ΣCO_2. Nonetheless, experimental evidence on freshwater photosynthetic utilization of inorganic carbon indicates a strong relationship between physiological availability and the forms of ΣCO_2 (Wetzel and Hough, 1972). The ability to assimilate bicarbonate ions is highly variable among planktonic algae, macroalgae, and submersed angiosperms (see a most comprehensive review by Raven, 1970). Where this ability does occur, additional reactions are needed for bicarbonate assimilation which are not required for CO_2 assimilation. Active bicarbonate transport with dehydration in the cytoplasm apparently is required and is coupled to a similarly active stoichiometric hydroxyl efflux. Where aquatic plants have similar affinities for CO_2 and bicarbonate, utilization of bicarbonate generally occurs when bicarbonate concentration exceeds CO_2 by more than 10 times (Raven, 1970). Free CO_2 concentrations (about 10 micromoles) of most freshwaters and the sea are in equilibrium with the atmosphere; however, many freshwaters contain bicarbonate concentrations far in excess of 10 times that quantity. Equilibrium free CO_2, particularly in the common alkaline hard waters with a pH >8, is inadequate to saturate photosynthesis in plants adapted to utilize bicarbonate. As these waters become more productive, and in densely populated littoral zones of less productive lakes, pH is rapidly modified by metabolism on a diurnal basis (pH range from 6 to 10 per 24 hr) and can be associated with reduced carbon fixation and bicarbonate assimilation. There is no question that under stagnant conditions the shift to bicarbonate metabolism, as well as the increased pH, is associated with depletion of CO_2.

Bicarbonate assimilation in media of high pH assumes greater significance in larger aquatic macrophytes that morphologically have long diffusion paths. Moreover, many angiosperms with large intercellular gas lacunae refix CO_2 of respiration and photorespiration rather efficiently (Hough and Wetzel, 1972). The efficiency of refixation and photosynthetic efficiency of carbon fixation must be highly plastic, related in part to induced shifts to bicarbonate assimilation, and can significantly affect rates of net primary production (Wetzel, 1969; Wetzel and Hough, 1972).

In summary, evidence is available that, among the enormous diversity of concentrations and states of inorganic carbon in freshwaters, there exists a large number of situations where free CO_2 in equilibrium with the atmosphere may be inadequate for metabolism or indirectly inadequate as a result of chemical losses from the system. Although it is highly doubtful that inorganic carbon per se is seriously limiting to photosynthetic metabolism under most natural situations, physiological shifts to assimilation of bicarbonate at metabolic expense appear to occur rapidly. Possession of an affinity for bicarbonate is an adaptive advantage in a significant percentage of freshwaters, particularly for larger submersed angiosperms.

ORGANIC CARBON

Nearly all the organic carbon of lake water consists of dissolved organic carbon (DOC) and dead particulate organic carbon (POC). Almost universally the ratio of DOC to POC approximates 10 : 1 in both lacustrine and stream systems. DOC is defined rather arbitrarily in most studies by the practical necessity of fractionation of POC from DOC by filtration at the 0.5-μ level; hence DOC concentrations can include a significant colloidal fraction in addition to truly dissolved organic carbon. Although the living POC of the biota constitutes a very small fraction of the total POC, the metabolism of this biota mediates a series of reversible fluxes between the dissolved and particulate phases of detrital carbon.

The composition and sources of organic carbon are diverse and poorly understood. Production of dissolved and particulate carbon is, in part, a result of autotrophic or heterotrophic metabolism. Instantaneous measurements of the chemical biomass of DOC and POC, however, are highly biased toward the refractory components of detrital organic carbon that accumulate in freshwaters. The labile components cycle rapidly at low equilibrium concentrations but represent major carbon pathways and energy fluxes. Furthermore, in streams and most lakes, much of the detrital organic carbon, mostly dissolved, is of terrestrial origin. A majority of lakes are small with a high proportion of their surface area as littoral zone. Allochthonous and littoral sources of dissolved and particulate detrital organic carbon form major inputs to the lacustrine system and can markedly modify pelagic metabolism. In streams, major metabolic carbon pathways for processing dissolved organic carbon are by planktonic bacteria rather than benthic microflora (Wetzel and Manny, 1972a; Cummins et al., 1972). In the relatively static waters of lakes, greater rates of sedimentation displace a major portion of carbon metabolism to the benthos (Wetzel, Rich, Miller, and Allen, 1972). To approach the complex carbon cycle that dominates both the structure and function of lakes, one must have a complete representation of the productivity of all components of the ecosystem as well as an understanding of the origins and metabolism of detrital organic carbon.

DOC and detrital POC exceed the amount of organic carbon of the fauna, plankton, and bacteria manifold (e.g., Birge and Juday, 1926, 1934; Saunders, 1969; Wetzel, Rich, Miller and Allen, 1972). *Detritus* is here defined functionally as all *nonpredatory losses of organic carbon from any trophic level (including egestion, secretion, excretion, etc.) or inputs from sources external to the ecosystem that enter and cycle in the system (allochthonous organic carbon).* DOC is functionally the most important component of the detrital-carbon trophic structure and is detritus in the truest sense of the definition. This definition removes the highly artificial "particulate" constraint from existing definitions of detritus. Further, discriminating between detritus and its associated flora and fauna provides needed functional applicability to more general conditions when associated bacteria serve other system functions, such as regeneration of nutrients (e.g., CO_2, N, P) or when detritus is utilized in other ways (e.g., algal heterotrophy, losses by adsorption, and precipitation with $CaCO_3$ and other inorganic particulate matter).

Any attempt to analyze trophic detrital dynamics necessitates a functional separation between the dissolved and particulate phases, both in the annual treatment of carbon biomass and in understanding functional pathways of sources, utilization, and losses. Over the past 5 years, we have attempted to develop a carbon analysis on this functional basis for a hard-water lake, Lawrence Lake, southwestern Michigan. Major pools and pathways of carbon flux are illustrated diagrammatically in Fig. 1. Conspicuous in this treatment of detrital organic carbon are: (1) the central dominant pool of DOC; (2) three major sources of POC, allochthonous, the littoral zone, and the pelagic zone; and (3) the major areas of detrital metabolism, the benthic region, where a large majority of POC is decomposed in many lakes, and pelagic sedimentation and decomposition.

Lawrence Lake is a typical hard-water lake of small size (4.9 hectares), moderate depth (12.6 m), and relatively low productivity (see Wetzel, 1971). We will summarize only the salient points of the carbon budget and fluxes here. Details of annual cycles and experimental analyses have been presented in Wetzel, Rich, Miller, and Allen (1972) and in an array of papers discussed therein. Only the mean annual budgetary figures and flux values are given here for illustration of rates of carbon cycling in this freshwater system and potential extrapolation to others of differing structure and productivity.

The rates of net primary production for Lawrence Lake have been investigated in some detail, and they serve to illustrate the commonly ignored contribution of the sessile producers to total autotrophic production (Table 1). The littoral zone and its flora are rather poorly developed in this lake; the values in no way exaggerate their importance. Needless to say, the relative contribution of these components is highly variable among freshwaters and is enormously complicated by differences in lake morphometry and edaphic factors. If we scrutinize existing data for lakes carefully, however, certain generalities appear in relation to increasing nutrient fertility of lakes (Fig. 2). At a given latitude, maximum growth of phytoplankton increases progressively with increasing fertility, and the intensity spectrum of simultaneously interacting nutrient

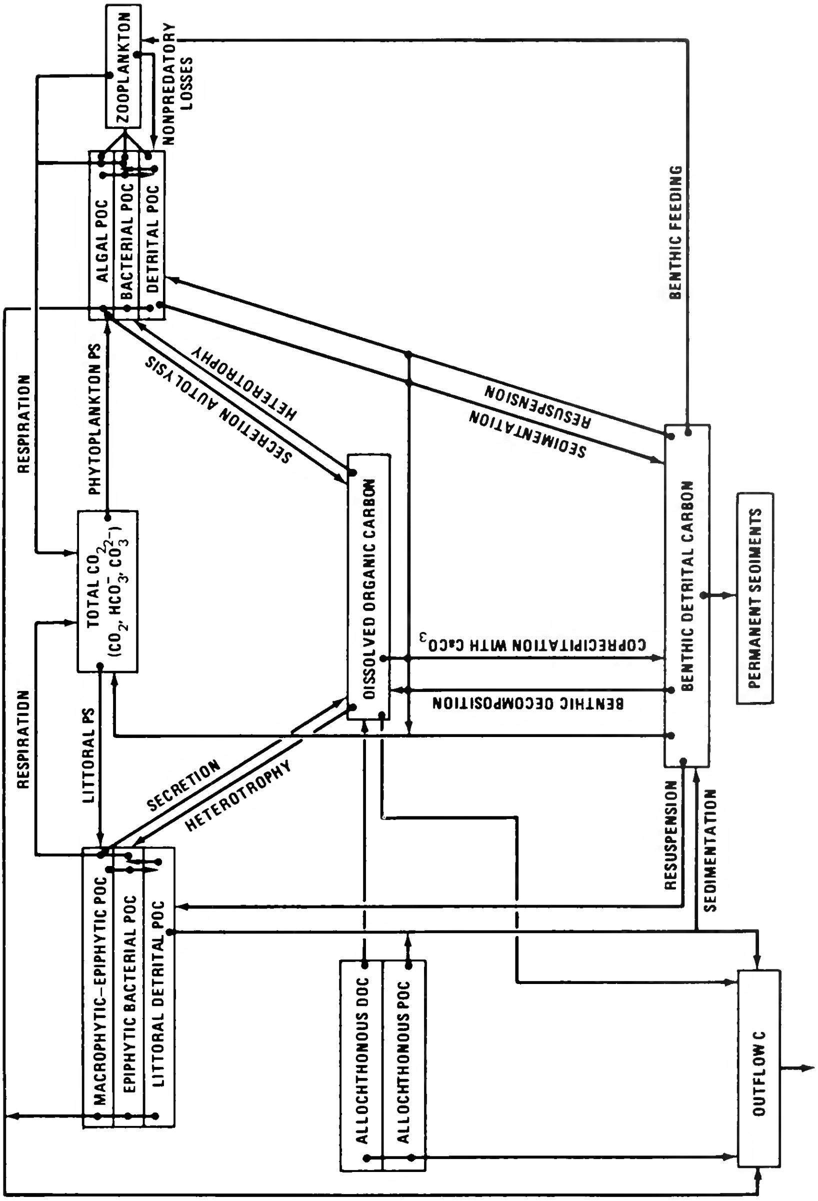

Fig. 1 Diagrammatic representation of dynamic structure of detrital carbon as modeled for a typical hard-water lake. DOC = dissolved organic carbon; POC = particulate organic carbon; PS = photosynthesis.

TABLE 1

RATES OF NET PRIMARY PRODUCTION OF PHYTOPLANKTON, EPIPHYTIC ALGAE, AND MACROPHYTES, LAWRENCE LAKE, MICH.

	Mean mg C m^{-2} day^{-1}	g C m^{-2} year^{-1}	
Phytoplankton			
1968	127.4	46.6	
1969	119.0	43.4	
1970	124.6	45.5	
1971	104.7	38.2	
Average	118.9	43.4	(25.4%)
Epiphytic algae			
Emergent substrates	196.0	2.9	
Submersed substrates	1807	35.0	
Sum	2003	37.9	(22.1%)
Epipelic algae		2.0	(1.2%)
Macrophytes	240.8	87.9	(51.3%)
Total for lake		171.1	(100.0%)

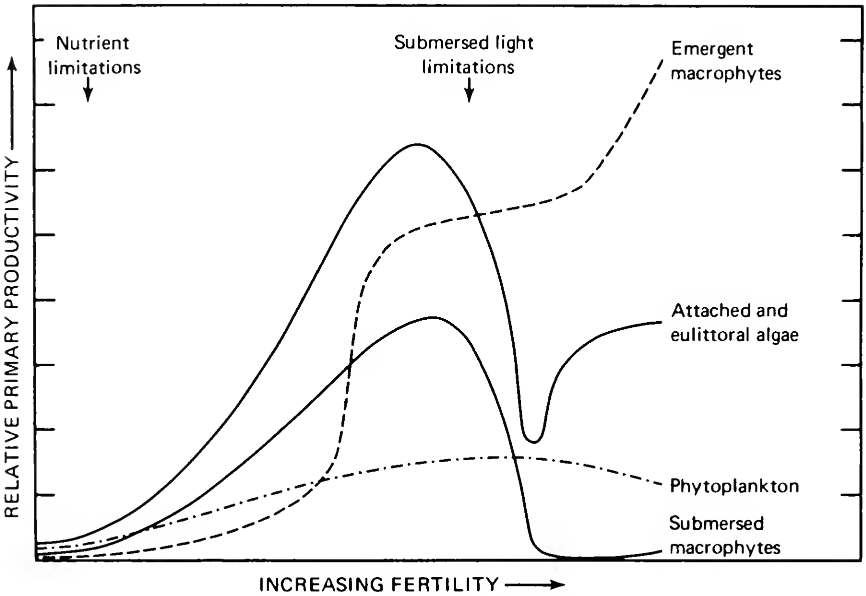

Fig. 2 Relative primary productivity of emergent and submersed macrophytic flora, attached and eulittoral (tychophytoplankton) algae, and phytoplankton in lake ecosystems of increasing fertility.

limitations decreases (Wetzel, 1971). A point is reached where population densities become self-limiting by self-shading effects beyond which growth can be increased further only by greater turbulence and light availability than occur under natural conditions (Wetzel, 1966).

Submersed macrophytes usually assume increasingly greater importance to the total autochthonous production of lakes (Fig. 2) until the fertility of the system reaches a point of severe light attenuation generally associated with biogenic turbidity of phytoplankton (Wetzel and Hough, 1972). Algae attached to the substrata or to macrophytes of less fertile sites commonly constitute a major, even dominant, site of organic-carbon synthesis. These sessile populations exhibit a population-growth stability not common among the phytoplankton.

As the emergent macrophytes assume greater dominance in lakes and eventually encompass a majority of the lake basin, an exceedingly productive combination of littoral macrophytes and attendant microflora develops (Fig. 2). Attached algae and algae loosely associated with the macrophytes (eulittoral algae; tychophytoplankton) develop strongly in association with the emergent flora.

The transitional stages of dominance in autotrophic productivity by phytoplankton, sessile submersed macroflora and microflora, phytoplankton, and then emergent macrophytes and associated microflora, as depicted in Fig. 2 and subsequent figures, are not intended to imply a succession of stages in the ontogeny of freshwaters. Some small lakes do evolve in relatively short periods through this general sequence; others do not (see Wetzel and Allen, 1972). Rather, within a nearly infinite spectrum of lakes, these general relationships among sites of relative primary productivity and increasing fertility of the systems are found. Many exceptions certainly exist.

The quantities of organic carbon released extracellularly by the primary producers of Lawrence Lake were relatively low (Table 2). Although the rates of secretion of DOC fluctuated to a marked degree spatially and temporally over an annual cycle, the mean percentage was about 5% of that carbon fixed in photosynthesis. Higher values have been reported in the literature, but practically no detailed annual means are available for comparison. High extracellular release of DOC during algal and macrophytic photosynthesis has been shown to be a function of CO_2 limitation, both high and low population densities, and both high and very low light intensities (Wetzel, Rich, Miller, and Allen, 1972). Greater secretion at the extreme ends of light and pH spectra indicate the operation of light and dark mediated secretion under different pathways (Fogg and Watt, 1966; Hough and Wetzel, 1972). Dark CO_2 fixation and secretion occur by numerous carboxylations, e.g., Wood–Werkman and Utter reactions, in which carbon enters four-carbon acids in the mitochondria rather than phosphoglyceric acid in the chloroplast, as in light-mediated Calvin-cycle fixation and secretion. This assumes no C_4 photosynthesis, which is probably true for both algae (Hatch et al., 1971) and submersed angiosperms (Wetzel and Hough, 1972).

TABLE 2

RELEASE OF DISSOLVED ORGANIC CARBON BY PRIMARY PRODUCERS, LAWRENCE LAKE, MICH.

	Mean photosynthetic carbon fixation, %	g C m^{-2} $year^{-1}$
Secretion		
Phytoplankton	5.7	2.7
Epiphytic algae	5	1.9
Epipelic algae	5	0.1
Macrophytes	4	3.5
Sum		8.2
Autolysis		6.5

TABLE 3

DISSOLVED ORGANIC CARBON, LAWRENCE LAKE, MICH.

	Mean g C m^{-2}	Mean kg C $lake^{-1}$
Pelagic zone		
1968	31.62	1570
1969	34.84	1729
1970	27.76	1378
1971	26.80	1330
Average	30.23	1502
	g C m^{-2} $year^{-1}$	
Allochthonous		
Inlet 1	7.00	
Inlet 2	7.94	
Groundwater and seepage	6.01	
Total	20.95	
Outlet	35.82	

Available evidence indicates that, in general, the percentage of photosynthetically fixed carbon secreted as DOC is greater in less fertile aquatic systems than in those more highly fertile. Since quantitative primary production is less in more oligotrophic waters, however, the absolute amount of DOC secreted is greater in more eutrophic lakes.

Although tne quantity of DOC secreted, in addition to that released by autolysis, is small in comparison to other sources (Tables 2 and 3), these organic substrates are labile (e.g., Wetzel and Manny, 1972b) and are subject to rapid heterotrophic utilization by bacteria (<48 hr) (Miller, 1972). In oligotrophic waters, labile DOC can be highly limiting to heterotrophic carbon metabolism and serves as a major factor among a number of simultaneous interactions suppressing productivity of freshwater systems (Wetzel, 1968, 1971). This labile-organic-substrate limitation, among an abundance of accumulated refractory organic substrates of very high residence times (turnover rates 1 to >100 years), can result from either an absolute deficiency in the system or abiotic loss mechanisms (such as adsorption to $CaCO_3$ as discussed previously or by sorption to mineral particulate materials (e.g., Bader, Hood, and Smith, 1960; Meyers and Quinn, 1971b). Once eutrophication and synthesis of DOC of the system proceeds to the point of continually saturating these inorganic sinks, heterotrophic metabolism increases relatively rapidly and can contribute significantly in accelerating nutrient (inorganic and organic) regeneration and the cycling of carbon (Wetzel and Allen, 1972).

The dissolved organic-carbon pool exhibits a relative constancy from year to year (Table 3). Maximum detrital biomass of DOC generally occurs in late summer and autumn, indicative of an accumulation of more refractory organic compounds prior to autumnal circulation of the lake. Highest values of DOC occur in the epilimnion, and concentrations consistently fluctuated more there than in the hypolimnion (see Wetzel, Rich, Miller, and Allen, 1972). These epilimnetic fluctuations are related to photosynthetic metabolism.

Biochemical origins and sources of DOC in such an ecosystem as Lawrence Lake are largely photosynthetic. In oligotrophic, moderately large bodies of water, phytoplanktonic photosynthetic metabolism dominates (Fig. 3). However, among a majority of lakes of the temperate region, of which Lawrence Lake is a typical example, the ratio of littoral to pelagic photosynthetic activity typically increases greatly as the mean depth of the basin decreases. Allochthonous inputs of DOC are quite constant for a given lake; their relative contribution to the system decreases as autochthonous sources increase. The ratio of photosynthetic fixation to dark CO_2 fixation and bacterial chemosynthesis is generally very large in oligotrophic waters. In Lawrence Lake, for example, the 4-year average of dark fixation was 16.3% of light fixation of phytoplankton (Table 4). The percentage is much less if the littoral photosynthesis is considered in addition to that of the phytoplankton. The ratio of photosynthetic to dark CO_2 fixation decreases markedly in the transition to planktonic eutrophy and hypereutrophy. With further transition of the system to dominance by emergent macroflora and associated attached and eulittoral microflora, the relative contribution of dark CO_2 fixation apparently decreases.

A detailed analysis of the heterotrophic utilization of DOC originating largely from phytoplanktonic secretion and autolysis in Lawrence Lake (Miller, 1972) indicates at least 44% of planktonic primary production was transferred

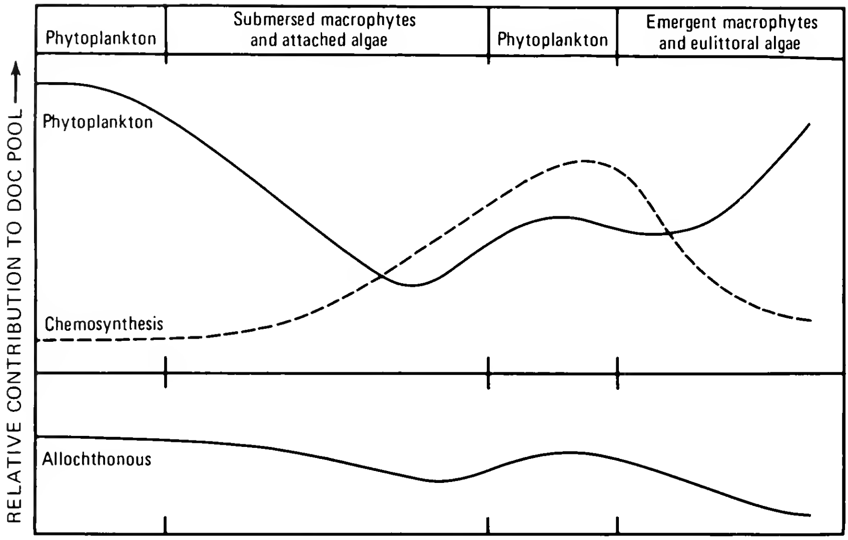

Fig. 3 Generalized relative contributions of phytoplankton, chemosynthetic dark CO_2 fixation, and allochthonous sources of dissolved organic carbon (DOC) to lakes of increasing fertility in the progression of dominating pelagic and littoral flora (see Fig. 2).

TABLE 4

CHEMOSYNTHETIC RATES OF DARK CO_2 FIXATION IN THE PELAGIC ZONE OF LAWRENCE LAKE, MICH.

	$g\ C\ m^{-2}\ year^{-1}$	Mean $mg\ C\ m^{-2}\ day^{-1}$	% of light CO_2 fixation
1968	5.0	13.7	10.7
1969	10.2	28.1	23.6
1970	8.0	22.0	17.6
1971	5.1	14.0	13.4
Average	7.1	19.4	16.3

through the DOC pool annually. This percentage likely decreases as systems become more eutrophic, particularly where littoral metabolism becomes dominant.

POC suspended in the water column of Lawrence Lake followed a conspicuously consistent pattern both seasonally (see Wetzel, Rich, Miller, and Allen, 1972) and from year to year (Table 5). Fluctuations in the POC pool closely paralleled those of phytoplankton primary productivity. A gradual

TABLE 5

PARTICULATE ORGANIC CARBON, LAWRENCE LAKE, MICH.

	Mean, g C/m^2	Mean, kg C/lake
Pelagic zone		
1968	2.1	102.8
1969	2.6	130.8
1970	2.2	108.3
1971	2.1	104.3
Average	2.3	111.6
	g C m^{-2} year^{-1}	
Allochthonous		
Inlet 1	2.0	
Inlet 2	1.0	
Groundwater and seepage	1.2	
Loess	0.0	
Total	4.2	
Outflow	2.8	
Sedimentation		
Of POC	32.8	
Of $CaCO_3$	196.4	

reduction in POC occurred under ice cover, a period during which primary production and allochthonous inputs were reduced. The relationship of approximately 10 times greater DOC than POC was very constant. The DOC to POC ratio of about 10 : 1 also existed in all lake waters in the region of Lawrence Lake, as well as in inlet streams and experimental and natural streams of the area.

Estimates of the replacement of algal-cell carbon in the pelagic POC can be made from the biomass of algal-cell carbon and the rates of net primary production. Compensating for respiratory loss of carbon (see Miller, 1972), the daily net accumulation of POC can be estimated from net primary production. Total suspended epilimnetic POC in Lawrence Lake had an average replacement time (turnover) of 40.7 days (range 8.1 to 544 days). Of this POC pool, a mean of 83.4 mg C/m^2 (range 30 to 241 mg C/m^2) was algal-cell carbon that was replaced by primary productivity in 1.06 days (range 0.30 to 2.55 days) during the ice-free seasons and with an annual mean of 3.6 days (Miller, 1972).

Generalizing on the cycling of organic carbon among phytoplankton populations is difficult because of the paucity of data, especially detailed annual cycles, under natural conditions. A few generalizations are apparent, however. POC concentrations of the pelagic zones are usually considerably larger (roughly

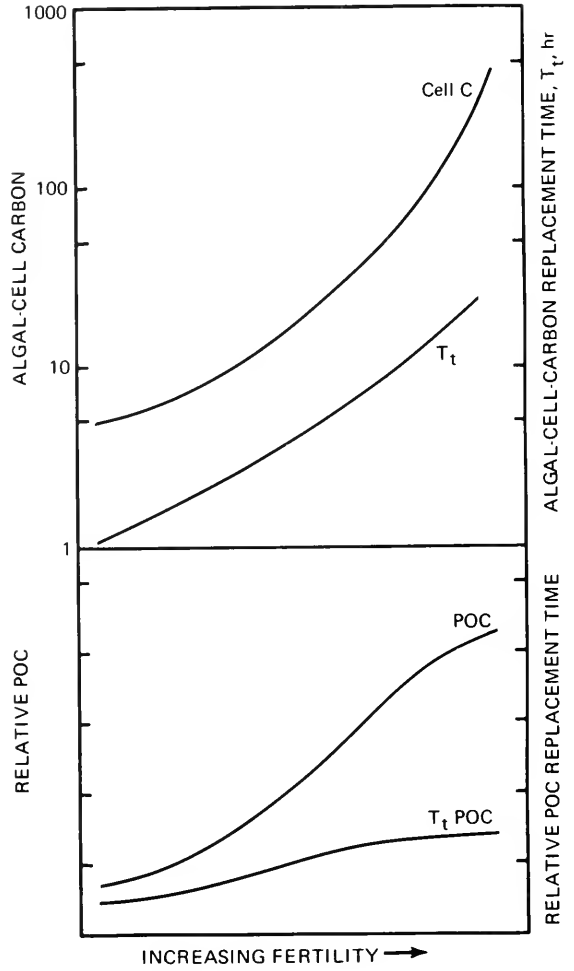

Fig. 4 Generalized relationship of pelagic algal-cell carbon and particulate organic carbon (POC), and their replacement times (T_t) in lakes of increasing fertility.

TABLE 6

ANNUAL BENTHIC PARTICULATE-CARBON BUDGET, LAWRENCE LAKE, MICH.

Inputs	
Submersed macrophytes	+87.9 g C m^{-2} $year^{-1}$
Epiphytic algae	+37.9
Epipelic production	+0.0
Sedimentation of POC	+21.7
Loess	+0.0
Precipitation of DOC with $CaCO_3$	+2.0
Outputs	
Benthic respiration	−117.5
Permanent sedimentation	−14.8
Balance	+17.2

double) in eutrophic lakes (Fig. 4). Differences in DOC are less marked in the transition from oligotrophic to highly eutrophic waters. Algal-cell carbon commonly increases nonlinearly with increasing fertility, with a slight tendency to algal cells of greater size. Replacement times of algal-cell carbon by net primary production are usually greater (slower turnover times) in eutrophic than oligotrophic waters but are not proportional to increases in cell carbon. Hence the algal cells are photosynthesizing more per unit cell carbon (have a greater carbon flux) in less fertile waters.

While planktonic metabolism of detrital organic carbon is very significant, especially in oligotrophic lakes, benthic metabolism of POC is of major importance. The annual estimate of benthic respiration for Lawrence Lake was 117.5 g C m^{-2} $year^{-1}$. Maximal values were found in the spring, and seasonal variations corresponded closely with littoral and pelagic productivity. Variations in rates of benthic respiration from the shoreline to the deepest depression of the lake correlated directly with biomass production of submersed macrophytes in all cases during the ice-free period (March to November). Benthic respiration was highest in the deepest sediments during the spring maximum of phytoplanktonic productivity (Rich and Wetzel, 1972).

The high rate of carbon flux as CO_2 from the sediments of Lawrence Lake was over twice the rate of carbon fixation by the phytoplankton (Table 6) and represents a good estimate of overall lake productivity since benthic metabolism tends to integrate all sources of carbon production. The sources of POC obviously shift their relative contributions to the POC pool as the freshwater systems frequently progress through stages of increasing fertility (Fig. 5). Again, it is difficult to generalize because of the high degree of lake individuality, but the importance of littoral components manifests itself within the overall

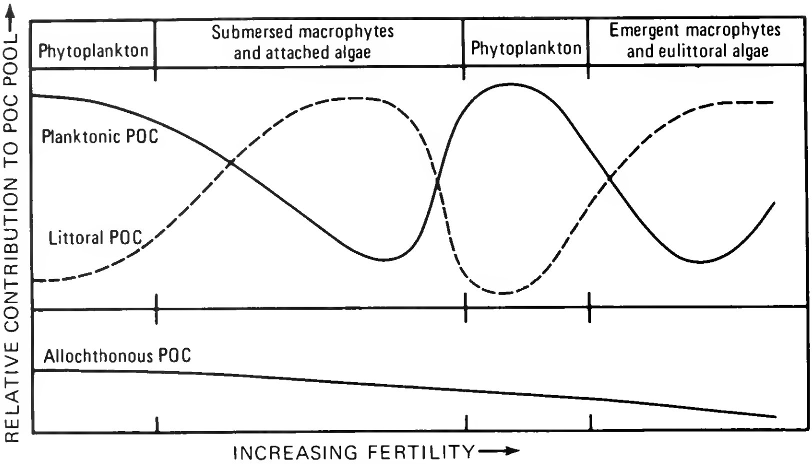

Fig. 5 Generalized planktonic, littoral, and allochthonous sources of POC to lakes of increasing fertility, with shifts in the domination of pelagic and littoral productivity (see Fig. 2).

transition from nutrient-limited conditions of oligotrophic lakes to light limitations of biogenic origins and dominance by emergent flora community.

In conclusion, the organic-carbon budgets for Lawrence Lake can serve in exemplary fashion to illustrate the various inputs, losses, and utilization relationships of organic carbon. The pelagic organic-carbon budget (Table 7) indicates losses of DOC exceed considerably inputs, resulting in a net production of DOC of -17 g C m^{-2} $year^{-1}$. In contrast, particulate-organic-carbon production exceeds losses (about 20 g C m^{-2} $year^{-1}$) and results in a total organic net production of $+3$ g C m^{-2} $year^{-1}$ for the pelagic zone.

In need of reiteration is the importance of the littoral region, not only its contribution to autochthonous production of the lake as a whole but also its indirect effects on pelagic and benthic carbon metabolism (Table 8). These estimates for the littoral organic-carbon budget of Lawrence Lake, based on a lake-wide area rather than an arbitrarily defined littoral zone, emphasize the magnitude of these components in the lake system. The characteristics of this lake are such that in no way is the littoral zone exaggerated. In a majority of lakes, the littoral contribution is a major component of organic-carbon flux.

NET ECOSYSTEM PRODUCTION

Woodwell and Whittaker (1968) originally defined net ecosystem production (NEP) as

$$\text{NEP} = \text{GP} - [\text{Rs}_{(\text{A})} + \text{Rs}_{(\text{H})}]$$

TABLE 7

PELAGIC ORGANIC-CARBON BUDGET, LAWRENCE LAKE, MICH.

DOC	g C m^{-2} year^{-1}	POC	g C m^{-2} year^{-1}
Inputs		Inputs	
Algal secretion Algal autolysis	14.7	Phytoplankton Resuspension	43.4 17.2
Littoral secretion		Allochthonous POC	4.1
Macrophytes	3.5	Bacteria	
Epiphytic algae	1.9	Chemosynthesis	7.1
Epipelic algae	0.1	Heterotrophy of DOC	7.4
Allochthonous DOC	21.0	Total	79.2
Total	41.2		
Losses		Losses	
Outflow	35.8	Outflow POC	2.8
Coprecipitation with $CaCO_3$	2.0	Sedimentation	21.7
Total	37.8	Total	24.5
Gross production	+3.4	Gross production	+54.7
Respiration		Respiration	
Bacteria (estimated as 50% of DOC production)	−20.6	Algae	13.0
		Sedimentation POC	21.7
		Total	−34.7
Net production	−17.2	Net production	+20.0

Total net production (DOC + POC) = +2.8 g C m^{-2} year^{-1}

TABLE 8

LITTORAL ORGANIC-CARBON BUDGET, LAWRENCE LAKE, MICH.*

	g C m^{-2} $year^{-1}$
Inputs	
Macrophytes	87.9
Epiphytic algae	37.9
Epipelic algae	2.0
Heterotrophy	2.8
Resuspension	0.0
Total	130.6
Outputs	
Secretion	5.5
Gross productivity	125.1
Benthic respiration	117.5
Net productivity	+7.6

*Estimates are on a lake-wide-area basis rather than on an arbitrarily defined "littoral zone."

where GP = gross production
$Rs_{(A)}$ = respiration of autotrophs
$Rs_{(H)}$ = respiration of heterotrophs

More recently Woodwell, Rich, and Hall (1972) modified the original expression to account for import and export of organic material:

$$NEP = (GP + NP^{1}_{in}) - [Rs_{(A)} + Rs_{(H)} + NP_{out}]$$

where NP^{1}_{in} = net production from another ecosystem
NP_{out} = net production exported

Both formulations interpret NEP as the net positive or negative increment of organic matter, either living biota or dead organic storage, after total respiration within the ecosystem. The latter definition of NEP, which specifically subtracts organic exports, limits the application of the term to only that material which remains inside ecosystem boundaries. Our experience with the Lawrence Lake study leads us to conclude that the original definition of NEP (Woodwell and Whittaker, 1968) is the more generally useful when considering aquatic situations (Table 9).

Aquatic systems appear to have much more dynamic equilibria than forest ecosystems, the context in which the term NEP was originally defined. In aquatic systems the biotic (living) structure is small compared to annual

TABLE 9

NET ECOSYSTEM ORGANIC-CARBON BUDGET, LAWRENCE LAKE, MICH.

	DOC	POC	Total
Inputs			
Inlet 1	7.0	2.0	9.0 g C m^{-2} year^{-1}
Inlet 2	7.9	1.0	8.9
Groundwater	6.0	1.2	7.2
Total	20.9	4.2	25.1
Outputs			
Outflow	35.8	2.8	38.6
Sedimentation		14.8	14.8
Total	35.8	17.6	53.4
Net ecosystem production (NEP)			+28.3 g C m^{-2} year^{-1}

productivity, and turnover is very high. Thus the NEP equation is an awkward way to ascertain the status of the biota. Furthermore, much aquatic productivity quickly enters the detritus pool, which represents the vast bulk of organic carbon in water, i.e., dissolved organic carbon. The turnover of this storage pool is also high, and unresolved estimates calculated by the NEP equation are relatively meaningless. As discussed here and by Wetzel et al. (1972), a detrital–dynamic structure exists in aquatic ecosystems which parallels the trophic–dynamic structure (biota) originally described by Lindeman (1942). Much of the detrital material in flux through this system is, indeed, respired to CO_2 by various elements of the biota and falls into the respiratory categories $[Rs_{(A)} + Rs_{(H)}]$ of the NEP equation. The operation of at least two phenomena associated with detrital–dynamic structure are recognized, however, for which the term NEP may be legitimately and very usefully applied.

Detritus as a Component of the Environment

A detrital–dynamic equilibrium exists for both the dissolved and particulate phase of detritus in natural waters at which rates of production and utilization are equal. This concentration has its own impact upon the chemical and physical milieu. Examples include the adsorption and coprecipitation of dissolved organic matter and $CaCO_3$ in hard waters and the formation of organic aggregates. In the Lawrence Lake case, a rather large amount of DOC is lost with the export of water through an outlet stream. Although this is certainly organic export, it actually represents another dimension of the dynamic situation within the lake where production is closely tied to factors contributed from the watershed (Wetzel, 1970), and export is similarly tied to the physical flow of water through the system by the rather constantly maintained equilibrium concentration of DOC. Thus export in this system represents the superimposition of a rather stochastic hydrology and homeostatic factors regulating both production and DOC concentration. The arbitrary exclusion of "export" from NEP in this situation is a gross oversimplification that obscures the operation of important regulatory functions of the ecosystem.

Detrital Electron Flux

The value of the original NEP formula is also seen in the case of a second phenomenon where the application of NEP to noncarbon substrates may be conceptualized. This is the special case of a detrital food chain wherein detrital energy is subsequently transferred by noncarbon substrates in an anaerobic environment. Because of the low solubility of oxygen in water, oxygen is frequently exhausted as an electron acceptor during hypolimnetic and benthic heterotrophy. The concentration of electrons then increases in the environment, and the redox potential becomes negative. Alternate electron acceptors, e.g., SO_4^{2-} and NO_3^-, are reduced by continued bacterial activity and are converted, in general, to more soluble products. Ferric iron may also be reduced to ferrous iron with a resulting decrease in the binding capacity of the sediments. The diffusion interface between the reduced products and dissolved oxygen then becomes the site of chemosynthesis where bacterial metabolism, actually noncarbon heterotrophy, reoxidizes the substrate. The term "detrital electron flux" reminds us that electrons, not carbon, represent the actual continuity in this case and are the ultimate trophic medium of exchange following photosynthesis.

In the case of anaerobic respiration, the NEP equation is misleading in terms of carbon because, although the carbon reduced in photosynthesis is oxidized, the oxygen oxidized in photosynthesis is not the substrate reduced:

$$CO_2 + H_2O \overset{\text{PS}}{\text{------}} CH_2O + O_2 \rightarrow \text{respiration}$$

$$\text{Aerobic} \rightarrow CO_2 + H_2O \qquad \begin{cases} \text{NEP} = CH_2O - CO_2 = 0 \text{ (carbon)} \\ \text{NEP} = O_2 - H_2O = 0 \text{ (oxygen)} \end{cases}$$

$$\text{Anaerobic} \rightarrow CO_2 + H_2S + O_2 \begin{cases} \text{NEP} = CH_2O - CO_2 = 0 \text{ (carbon)} \\ \text{NEP} = O_2 - H_2S \neq 0 \text{ (oxygen)} \end{cases}$$

It may be argued that H_2S is ultimately equivalent to H_2O; however, energetically there is a discrepancy equivalent to the distance between oxygen and sulfur in the electromotive series. This discrepancy is manifested in the inequality of the NEP equation for oxygen.

The NEP concept is a powerful insight, open to much elaboration. In the final analysis its unique usefulness derives from its compatibility with both material and energy units and with both trophic and compartmental models of ecosystems. Although the role of detritus in ecosystems is complex and poorly understood (Wetzel et al., 1972) and the current definition of NEP (Woodwell et al., 1972) is inadequately resolved, we believe the original NEP concept to be a valuable tool in the ultimate elucidation of carbon and energy ecosystem dynamics.

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DISCUSSION BY ATTENDEES

Caplan: Your estimate of maximum gross production for Lawrence Lake is 8 g C m^{-2} $year^{-1}$. Ryther predicts 6 g for artificially enriched aquatic systems; Japanese work has demonstrated a potential maximum of 16 g during short periods of less than 3 months. How would you compare the potential gross primary production of freshwater for agriculture to marine systems as described by Ryther utilizing tertiary sewage effluent as a nutrient source?

Wetzel: My general reaction would be that freshwater systems would have a higher production. My conclusion is based on the higher organic concentrations found there, as well as on higher nutrient inputs from surrounding land.

Olson: The words we use to describe things in biology greatly affect how we think about them. On the basis of the papers of both Riley and Wetzel, it seems to me that the term "dissolved organic carbon" is highly unsatisfactory as presently used. The term "colloidal organic carbon" should be introduced to denote those forms of carbon which will pass through a filter but which will not pass through a cell membrane under any circumstances.

Wetzel: I agree.

Baylor: It is obvious that the speakers here today are all aware of the problem, but I think that the arbitrary use of "filtration" as a definition for what is dissolved and what is not dissolved organic carbon is a kind of procrustean bed upon which many investigators have been led astray.

Livingstone: Richardson, Melack, and Kilham have been measuring production in some rather unusual closed-basin lakes in East Africa. The country rock around the lakes consists of readily soluble volcanics rich in nepheline, and the sump lakes at the downstream end of the groundwater flow have high concentrations of all the elements of which planktonic organisms are composed. The productivity is very high, apparently between 3000 and 4000 g C m^{-2} $year^{-1}$, and the lakes are dominated by phytoplankton. The 99% extinction level for light lies at a depth between 1 and 10 cm, and even germinating aquatics with large seeds seem unable to grow up to the surface before they run out of stored resources. Taking into account the whole spectrum of lake productivities then, one finds a third phytoplankton-dominated peak.

This is an example of the sort of difficulty one gets into by using Liebig's Law of the Minimum in biology—it is not operationally definable, and there is no feasible experimental method by which Liebig's sort of "limiting factor" can be identified. In lakes with such a tremendous supply of nutrients as these African ones, the rules of the productivity game are fundamentally altered, and the phytoplankton comes very close to using all the available light of appropriate wavelength in photosynthesis.

IS THERE INTELLIGENT LIFE ON EARTH?

PRESTON CLOUD
Department of Geological Sciences, University of California, Santa Barbara, California

This paper is about man's place on an evolving earth, about some of the constraints that limit our choices in the occupancy of this earth, and about steps that we might take to keep our options open. "The times, they are a-changin' " says a well-known Bob Dylan song, and we are going to need bigger changes and more of them before long. In a very deep sense, our times began "a-changin' " with the insights of Copernicus, Kepler, Newton, and Darwin which brought about man's dethronement from his position as the epitome and center of creation and caused him to begin asking a lot of questions about himself and his relation to the universe. Among the questions asked most frequently and most persistently is the question: Is there life elsewhere in the universe? And, if so: Might there even be intelligent life elsewhere, perhaps on some other planet to which man might move after filling this one up? It is interesting in looking at this question to turn it around and ask: What is the evidence for intelligent life on Earth?

Consider the views we have now seen of Earth from space. We can all see it in our mind's eye—a tiny, fragile speck in the dark emptiness of space, essentially a closed system. This is a picture of the earth that man in general has never really grasped until recently, despite the warnings and the urgings of generations of ecologists. Suppose now, to get things into perspective, that you were an inhabitant of another planet, a planet with an atmosphere but without free oxygen. Imagine that you had somehow managed to evolve into an observing, reasoning being with an anaerobic metabolism. Assume further that in the laboratories on your planet there had developed an understanding of the origins of life comparable with that now existing on Earth and, in addition, that spectroscopic and other remote sensing devices based on your planet have told you that there is about 20% oxygen in Earth's atmosphere. You would conclude that there could be no life on Earth—oxygen being poisonous to all forms of life in the absence of suitable oxygen-mediating enzymes of which you would have no knowledge. You would probably also conclude that life could not have arisen on Earth in the past—oxygen being destructive to all large molecules of which living organisms might be made. Of course, you would be wrong. There is life on Earth, perhaps even intelligent life.

We might consider another way of looking at Earth and its inhabitants, a way that I owe to the lively imagination of a good friend, the great biologist Paul Weiss of Rockefeller University and other places. Weiss (1965) has written an interesting fantasy about a visit by a Martian observer to Earth. The Martian spaceship arrives in the evening just as many vehicles are moving toward a drive-in theater for the night's entertainment, and it descends to observe these curious wheeled creatures moving along smartly in rather striking stop-and-go patterns, apparently governed by some master mind that flashes signals in red, yellow, and green. The observer follows them to the drive-in theater where he is able to get down a little closer as they huddle in formation before the flashing superintelligence. He there identifies their squirming occupants as internal parasites. Later, when the evening's ceremony breaks up, and the curious wheeled earthlings take off from the drive-in theater, the Martian observer is excited to see what appears to be some kind of sacrificial mating act, consummated when two earthlings rush together at high speeds, become intricately entangled and are hauled off by other earthlings and their internal parasites to be reconstituted as shiny new earthlings.

But let us be serious. Consider some of the more obvious manifestations of life on earth that might be revealed to the remote sensing devices of an exploring spacecraft from another planet. Prominent among these would be curious geometrical configurations characterized by high thermal, hydrocarbon, and radioactive concentrations and linked together by radiating linear networks rich in the same components, plus lead, mercury, and other trace elements of biological interest. What might a Martian observer conclude about this? Might he think that he had arrived on the scene at a late stage in the degeneration of earthly life or, by analogy with J. R. R. Tolkien's "hobbit" fantasy, that he had arrived at the moment that evil forces radiating out from local strongholds were about to overwhelm all that once had been wholesome in Middle-Earth.

Well, let me be explicit. My theme is that man is fast approaching a crucial test of one of the great universal generalizations—of Le Chatelier's principle, which states that, whenever a system in equilibrium is disturbed, it tends to react in such a way as to restore the equilibrium. Of course, we are all aware that equilibrium outside of a test tube is a will-o'-the-wisp thing. What we really mean is a condition of steady state or dynamic equilibrium, a condition that is always evolving but wherein things tend to remain more or less in balance. The question is whether man will come into balance with his ecosystem as a result of conscious thought and deliberate action, which he is perfectly capable of doing, or whether he will leave matters to the operation of the often catastrophic forces with which nature eventually brings all living beings into balance within the global ecosystem. The answer to that question is the answer to the question that titles this paper: "Is there intelligent life on Earth?"

Just what are the characteristics of the global ecosystem that impose limits on its use and abuse? First is the indivisibility of the environment. Hardin (1959) has phrased this as "you can't do only one thing." Whatever happens to any part of the environment has repercussions on other parts of it—not only on adjacent parts but in some sense eventually on all other parts of the whole ecosystem. A second limiting characteristic of our global ecosystem is the impossibility of continued exponential growth within it. Nothing can increase infinitely in a finite system. This is the crux of the Malthusian doctrine—often maligned but never invalidated. Another factor that constrains our flexibility of choices has to do with the idea that a sequence of actions, each individually justifiable on the basis of evidence on which a particular action is taken, may have cumulatively adverse effects.

Let us begin our examination of the ways in which the limiting characteristics of our global ecosystem are being tested with a look at the growth of world populations through the Christian Era (Fig. 1). Graphically this takes the form of a typical exponential curve with a doubling time that for the world as a whole is now about 35 years. With the advent of the industrial revolution and modern medicine, the doubling times have been getting shorter and the quantities larger. In the lower right-hand corner of Fig. 1 is shown one possibility for the way the industrial era may eventually look to our descendants in the historical perspective of hundreds or a few thousands of years hence. If present trends of population growth and rising consumption of material goods continue without leveling off and coming into some kind of equilibrium, they must eventually reach a peak and descend on the other side. We may all hope, of course, that this is just an alarmist nightmare and that it will not work out that way, but to avert such a peaking and collapse is likely to require conscious effort on our part both to stretch the limits of the ecosystem within reason and to accommodate ourselves within those limits where their stretching is impossible or inadvisable.

Figure 2 illustrates a distinctive index of the industrial revolution which coincided with the rapid increase in global population—pig-iron production. Increase in production of pig iron and other mineral commodities made possible increases in nearly everything else. Mechanization grew; farms became more efficient; we could feed more people; and larger labor forces were needed for more factories, plantations, and agencies to produce more of all kinds of goods and services. Figure 2 shows the growth of pig-iron production, which, for the world at large, has now reached about 400 million metric tons/year. The various lines for nations and the world as a whole reflect the vagaries of war, depression, and national fortune. You can see that the present leading producers of pig iron, in order of rank, are:

1. The USSR, which passed the United States during the last year.
2. The United States.

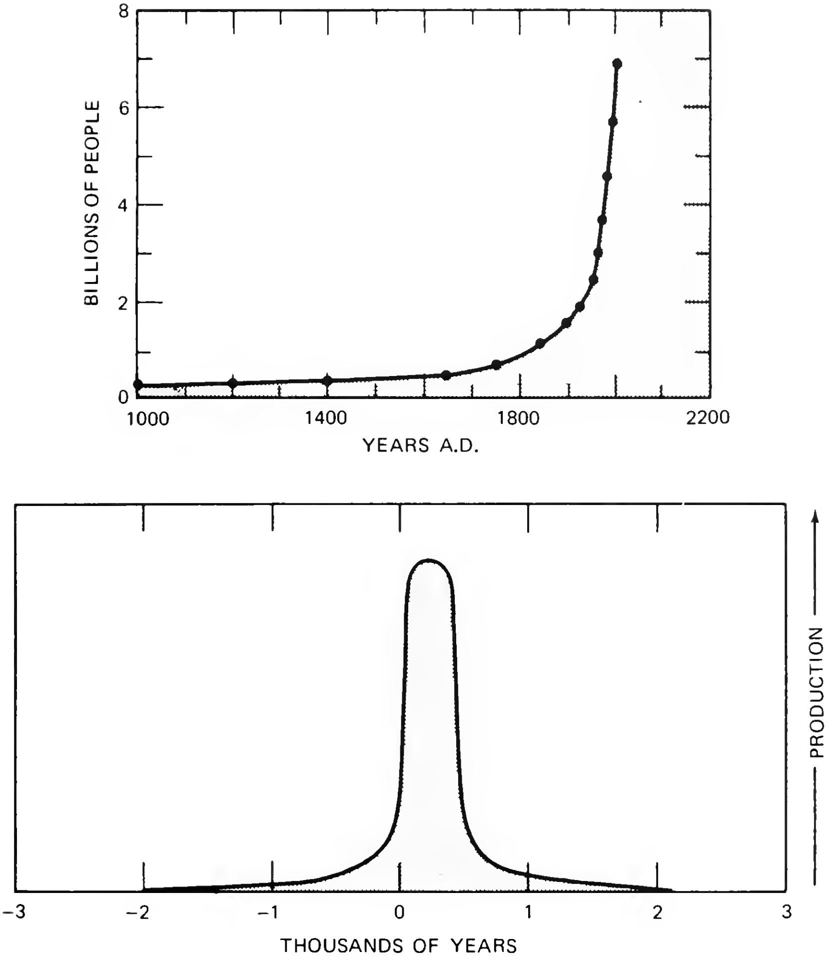

Fig. 1 Population growth to date compared with a retrospective model of the industrial era in historical perspective [inspired by Hubbert (1969), Fig. 8.27].

3. Japan, which is pressing hard on our heels, and almost entirely with imported materials.

That sets the stage for considering just how far industrial civilization can grow in any country or in the world at large without consequences that undo the good it is capable of creating, given appropriate controls.

Now a few words about concepts of optimum population and of quality of life, both of which are involved in my thinking. Is there such a thing as an optimal population, and, if so, what is it for different parts of the world and for the world as a whole? How does one define "quality of life," which, in concrete terms, surely means different things to different people? I would define

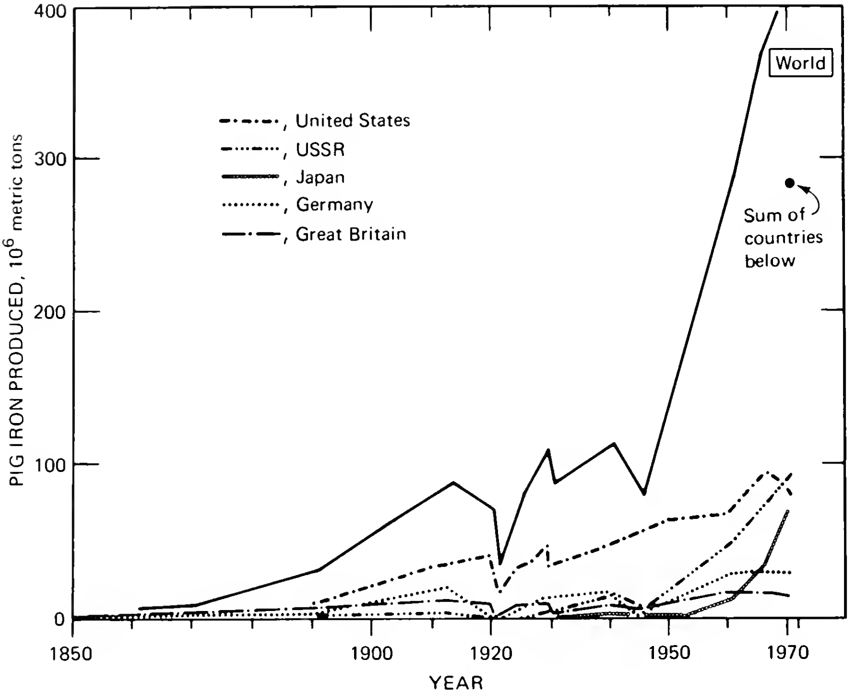

Fig. 2 **World pig-iron production (data from the U. S. Bureau of Mines** ***Minerals Yearbook*** **and the** ***Encyclopaedia Brittanica*****).**

an optimal population as one that is large enough to realize and utilize the full capabilities of man to generate a life of high quality for all people everywhere but not so large as to threaten that quality or the emergence of the inventive genius which is needed to create it. I would define quality of life as being a function of the variety and flexibility of options available. Anything that threatens or limits these options or restricts our ability or that of posterity to exercise them threatens the quality of life.

It is very hard to put meaningful numbers on such things, but I have tried to create a sense of what is involved by inventing an index that I call the Demographic Quotient, Q. I define Q as being given by total resources available on a continuing basis divided by population times per capita consumption: $Q = r/pc$. No matter how else we may prefer to detail our individual concepts of "quality of life," there is some general relation here that is worth thinking about. If we could define some minimal level of consumption that went along with a life of high quality, and if we knew the total resources available on a sustained basis, then we would know the size of population that would be sustainable given a fixed level of Q. You can also see that it is possible to keep Q constant by changing the variables on the right side of this equation. You can increase the total resources available; or you can increase the death rate, decrease the birth rate, or decrease per capita consumption. I think it is also clear that, given the choice in those terms, the fact that rates of population growth have not already fallen to bare replacement levels is evidence that not enough people are able to exercise the choice or that not enough of them understand the choice to be made.

Let me tell you where we stand now, with reference to population and consumption. As late as the year 1950, when more than one-third of the world's present population and one-quarter of that of the United States was not yet here, the imminence of the problems now facing us was not at all clear. A few farsighted people saw difficulties ahead, but to most people it seemed that there was plenty of room not only in North America but elsewhere in the world, plenty of resources, and no great hazard to the environment. Since 1950 the U. S. population has grown by about 56 million—the gross national product (GNP), which was then $400 billion, has increased by two and one-half times to a trillion dollars in 1971, and solid wastes have reached a total of about 4 billion tons/year. About 400 million tons of these solid wastes are urban—a great mixture of trash, paper, tin, garbage, and whatnot which could be segregated and used in some way. About 1.6 billion tons of it is solid wastes produced by mining, along with the various acid mine waters and other liquid wastes that go into the environment, and about 2 billion tons of it is agricultural wastes. It is incredible that we do not use more of these wastes constructively. We must learn to manage these wastes and, insofar as possible, convert them to resources. But these figures also provide a measure and a warning of the way the problem is increasing and cautions us about continuance of the exponential growth curves that many see as undergirding all progress. For, contrary to early 1972 newspaper accounts stating that the latest census figures indicate an approach to zero population growth, the fact is that our rate of population growth in May 1972 is about 0.97%, which means a 72-year doubling period for the population of the United States.* Add to this a 17-year doubling period for the GNP, now over one trillion dollars for the United States and three trillion for the world, and think what the problem will look like at the turn of the century.

But how about material resources? Will their availability eventually limit populations if pollution or malaise does not get us first? When I speak about material resources, I refer to two kinds of resources—renewable resources representing food, forest products, and water and such nonrenewable resources as mineral resources, especially mineral fuels and metals. I am, of course, not totally ignorant of thermodynamics. I am aware that the metal resources here called nonrenewable do not leave the essentially closed system that constitutes

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*The end of the 1972 census reports show U. S. fertility to have decreased to the level of bare replacement growth. This is encouraging. For reasons given in this paper, we should now try to reduce the level still further, at least until zero population growth is finally attained in the United States, while simultaneously encouraging similar salutary trends in the underdeveloped areas of the world.

the earth. They do, however, become dispersed, some of them irretrievably so through oxidation and friction, whereas others require energy and effort to recycle. In addition, exponentially increasing rates of consumption require the placing of ever-larger quantities of metals and other mineral resources into circulation. Human populations must eventually be limited in number, other limits not intervening, by the total sustainable annual crop of food and other renewable resources and by the total quantities of nonrenewable resources that can be put into circulation and kept there.

It would take too long to develop the arguments here, but they accompany estimates made by the National Academy of Sciences Committee on Resources and Man (1969) which I shall summarize. The estimates say, in effect, that, if all the inventiveness of man could be put to completely efficient use, if luck were with us, and if we did not worry too much about ecological trade-offs, the world might feed eventually, at bare subsistence level, as many as 30 billion people. Now 30 billion people sounds like an awful lot, especially since there are only 3.8 billion of us on Earth now, but it is the number of people that present rates of population growth would put on the earth about 100 years from now. It is doubtful that a nutrient increase of the needed dimensions can be attained within 100 years, if ever.

The nonrenewable resources are much harder to quantify. Except for a very few of them, we do not know absolute quantities available even within broad limits, and all sorts of variables affect our estimates. It is easier to look at this in terms of what quantities of nonrenewable resources would have to be put into circulation and kept in circulation to sustain the world population expected at the end of the century at a level of living comparable with that of western Europe. Again, without going into detail, but looking at different resources individually, we see that this turns out to be somewhere between 140 and 540 times the present annual rates of production for various critical commodities to be put into circulation in the next 30 years. It is very doubtful that this can happen, and the prospective environmental trade-offs are staggering! Thus the aspirations of the developing nations to achieve levels of living comparable to those of the now affluent have little hope of fulfillment in the near future, or ever, without sharp limitation of population and rates of consumption.

Consider now the cycle of materials in industrial society as shown in Fig. 3. Ultimately most of our industrial materials come out of the earth through mining, metallurgy, and mineral processing. Excluding energy raw materials, we start out with basic raw materials representing only about 1% of the GNP. By means of purification, fabrication, and recombination, with large inputs of energy, these basic raw materials are converted into refined raw materials. Through further processing, they are eventually brought up to final materials for various kinds of goods and services and the fabrication of products. At that point the materials, including the energy that has gone into upgrading them, represent about 40% of the GNP. So you see that even though the start is with a very small quantity—the vitamins or mineral raw materials of industrial

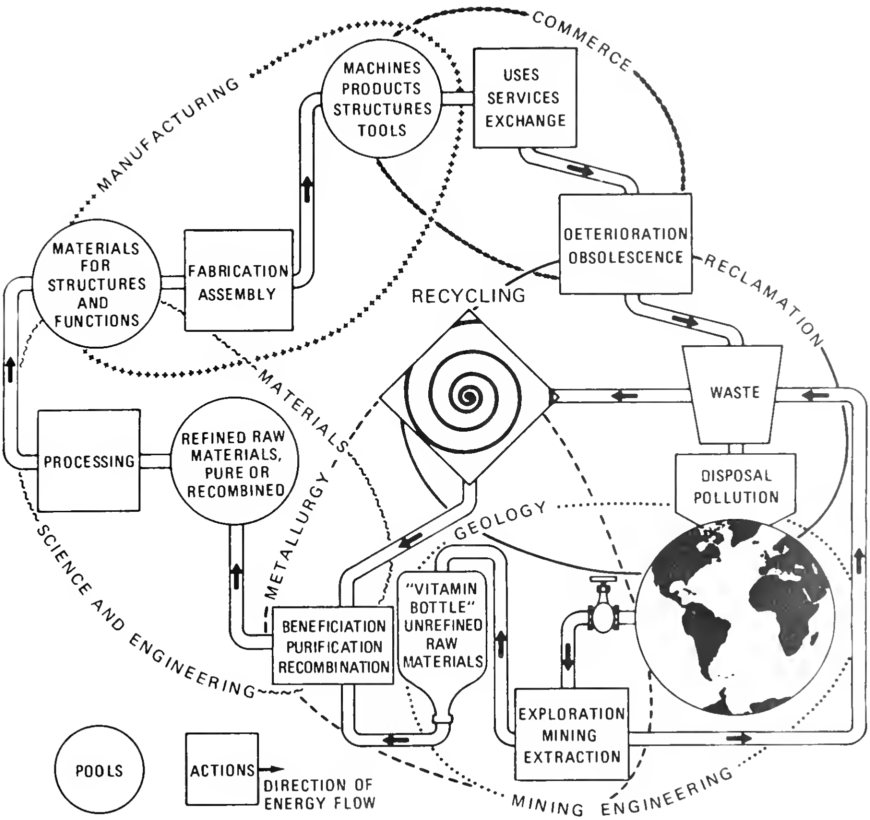

Fig. 3 Cycle of nonenergy materials in industrial society (inspired by a sketch by A. G. Chynoweth).

society—a strong multiplier effect on this quantity gradually upgrades it until it represents a major fraction of all the goods and services utilized. Finally the products, through various uses, deteriorate and become waste. This waste then either becomes pollution, returning to or into the earth, or is recycled, bypassing the raw-materials bottleneck and going back through the system again. One big opportunity for improvement is in recycling, but remember that the quantities needed are doubling every few decades or less because of exponential growth of consumption. Therefore, even if everything is recycled, it is still necessary to show at least as much new primary production for every doubling period. The effects of some of those exponentially growing demands can be seen in Figs. 4 to 6.

Figure 4 shows global reserves of selected critical raw materials compared with demand expected to the end of the century. This information is from the 4th edition of *Mineral Facts and Problems*, published by

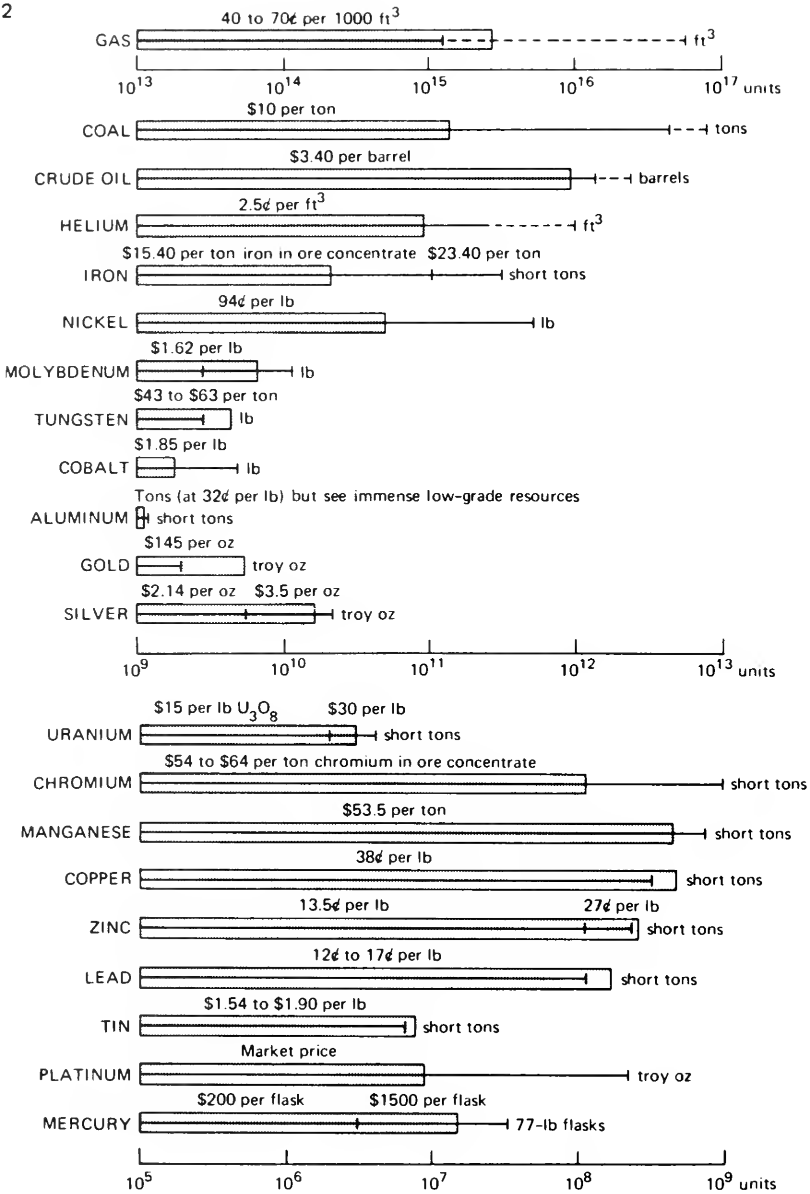

Fig. 4 Reserves of selected global mineral commodities compared with cumulative demand, 1968 to 2000. Scale is logarithmic; prices are in 1968 dollars; all lines have their zero points to left of chart; note variable nature of unit quantities. Data from U. S. Bureau of Mines (1970), supplemented by U. S. Bureau of the Census (1970) and Committee on Resources and Man (1969). The median lines show optimistically estimated reserves as of 1968, and the shaded boxes indicate cumulative demand, 1968 to 2000. Total reserves at different costs are indicated by position of vertical tick to right of cost per unit.

the U. S. Bureau of Mines (1970), and brings us up-to-date through 1968. Here the reserves of various commodities are shown by the thin horizontal bars in various appropriate units and scales. The scales of the various groups of bars go to larger exponents upward, and all project to zero off the page to the left. I have taken optimistic figures for reserves, often including those which will only become available at substantially higher than current prices or inferred beyond measured reserves, or both. Over these thin reserve lines are shown wider, lighter bars, indicating expected average global demand to the end of the century. Figure 4 also shows where reserves are and where they are not adequate to meet average demands expected to the end of the century. A good many are not adequate, although they may well be increased by discovery of yet undiscovered resources or mining of lower grades, as suggested by several reserve bars that show different end points for quantities available at different prices. Figure 4 represents the world as a whole. Figure 5 shows similar data for the United States.

From the same data, Fig. 6 shows, on a global basis, apparent mineral lifetimes, although not for quite the same group of commodities. For all commodities shown in Fig. 6, I have again used conservative estimates of demand rates and have looked at the apparent mineral lifetimes from 1968 onward in terms of three categories. The solid line on the left represents optimistically estimated current reserves, the dotted line in the middle gives the extended lifetimes for five times current reserves, and the solid line on the right represents an extension to 10 times current reserves. See where these lifetimes lead: We still run into severe shortages by the middle or end of the 21st century, some of them coming early on. How far we will be able to extend these resources is a matter not only of economics and technology but of the discovery, through application of geological principles, of presently unknown reserves. Although these variables are all uncertain, in the case of petroleum we can infer on rather good geological grounds that about five times currently known reserves of petroleum will be found, leading to a tapering off and decline in petroleum production beginning probably around 1990 to 2000. If we add oil shale and the so-called tar sands, then we are warranted in raising total reserves of petroleum-type products up to about 10 times those now known, although that is probably about as far as we can take petroleum. So you can relax and quit worrying about smog from gasoline by year 2040 or thereabouts. It will be gone or on a declining curve.

In the case of coal, the probability of about 10 times known reserves is pretty good, which takes us up to around 2150, although this will go much faster if it comes under heavy pressure to replace energy needed as crude petroleum and natural gas are used up. A longer range hope is to develop a clean breeder reactor and eventually a fusion reactor that will make available much larger quantities of energy. But then it will be important to have ample inventories of helium so that this energy can be transferred from its place of generation in superconductive lines without loss of energy en route and to

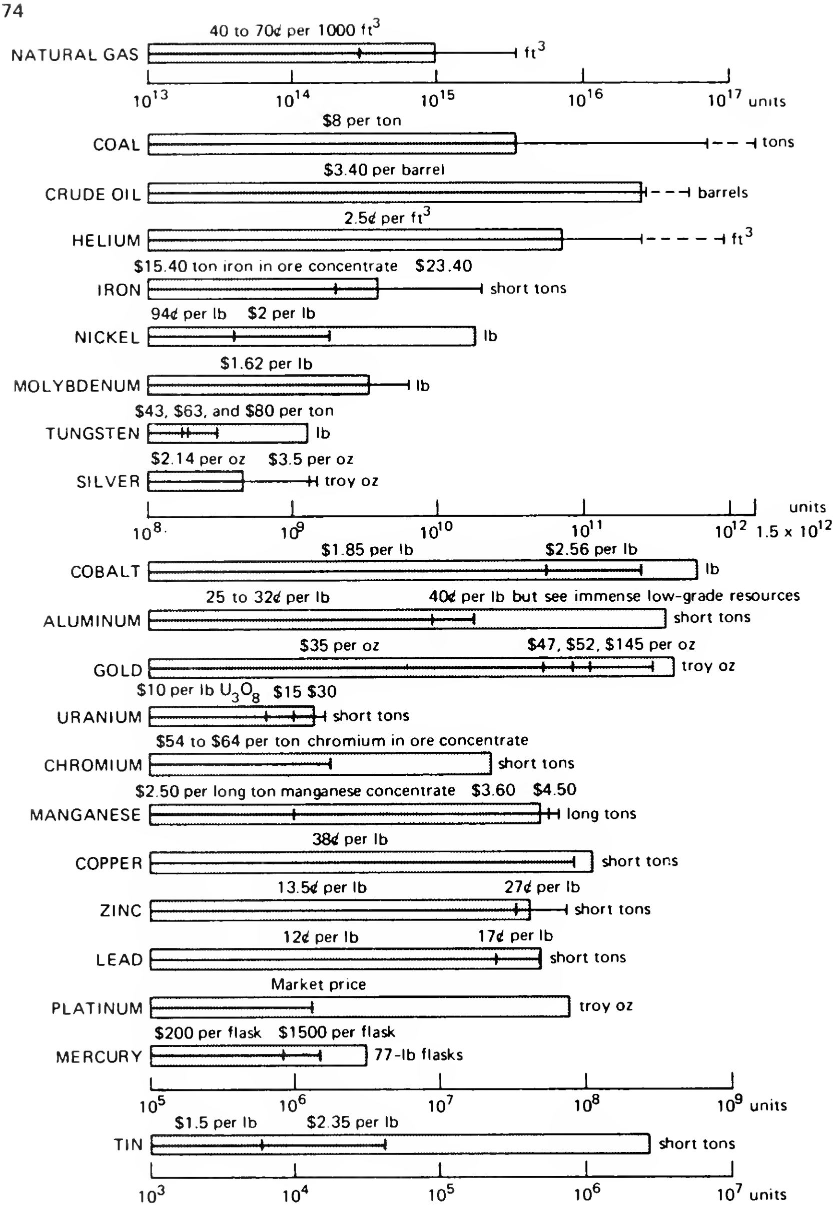

Fig. 5 Reserves of selected U. S. mineral commodities compared with cumulative demand, 1968 to 2000. Scale is logarithmic; prices are in 1968 dollars; all lines have their zero points to left of chart; note variable nature of unit quantities. Data from U. S. Bureau of Mines (1970), supplemented by U. S. Bureau of the Census (1970) and Committee on Resources and Man (1969). The median lines show optimistically estimated reserves as of 1968, and the shaded boxes indicate cumulative demand, 1968 to 2000. Total reserves at different costs are indicated by position of vertical tick to right of cost per unit.

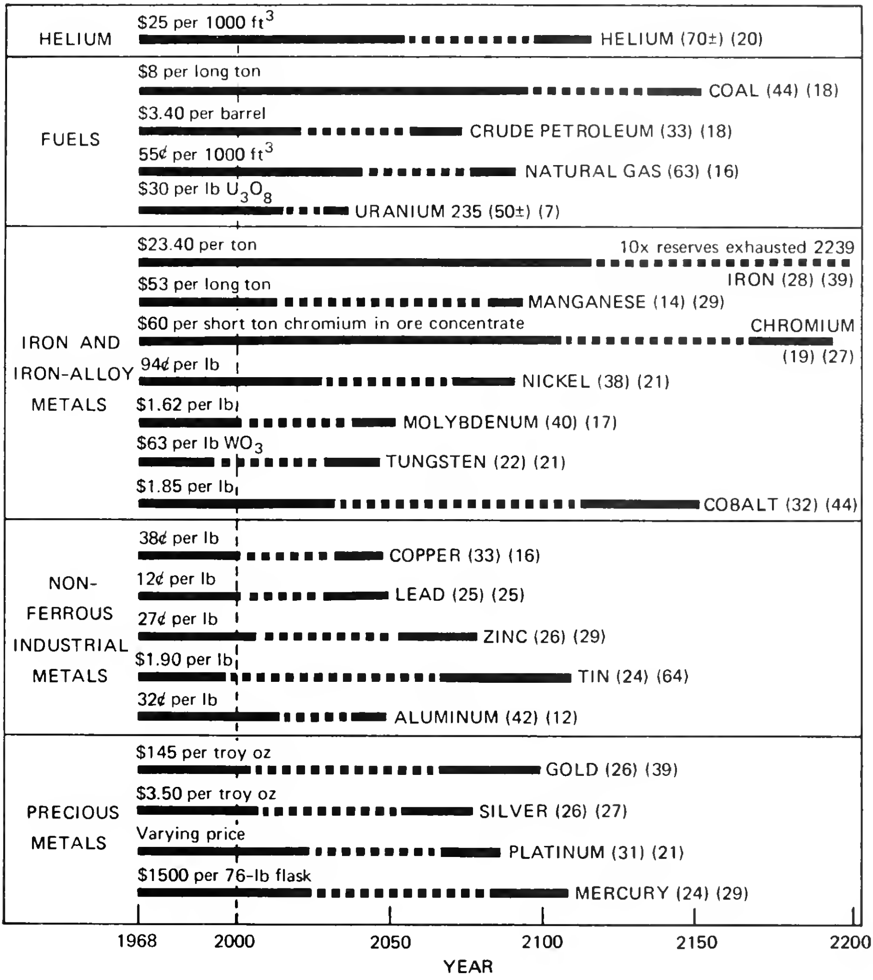

Fig. 6 Apparent lifetimes of optimistically estimated "reserves" of mineral commodities at expected rates of demand to year 2000. Solid line at left shows reserves at indicated prices (1968 dollars); dotted line at left indicates 5x these reserves; solid line at right indicates 10x estimated reserves. Numbers in parentheses are percentages of current world consumption by the United States (left) and current doubling rates of global consumption. Data from *Mineral Facts and Problems*, 4th ed., U. S. Bureau of Mines, 1970.

safeguard people and their environment against the substantial hazards of fission energy until contained fusion reactors become a reality.

What are the chances of increasing the reserves of now limited resources by more than an order of magnitude above those now known, and what would we gain or lose by doing so? What do we do to stretch the limits—to remain within our budget, as it were? The need to care for larger populations at better levels is inevitable. The age structure of the present population is such that, *even if we were to begin reproducing at bare replacement* from the present time,* the population of the earth as a whole would increase by 50% in the span of a human lifetime—that is, it would reach an eventual total of around 5.7 billion earthians by about the year 2040, while the population of the United States would still increase by about 35% over the same period of time, reaching an ultimate population of around 280 million. No matter what we do, therefore, short of going to the one-child or no-child family, we are going to have to care for a larger population, and we want to care for these inevitably larger populations at better levels of living. It does seem urgent to try to stretch the limits of supportability along with taking ever greater precautions to safeguard the environment and to limit population growth.

Consider some of the ways in which the limits might be stretched.

First, although overrated by many of its proponents, is nuclear energy. Nuclear energy helps in three ways:

1. It can lead to conservation of the fossil fuels that are really much too useful as sources of plastics and other petrochemicals to be burned. The faster we can move safely to deriving higher proportions of our energy budget from nuclear sources, the less pressure that makes on fossil fuels, permitting them to be conserved for other more versatile uses.

2. Nuclear energy will bring distant resources to the market place, either by lowering the costs of transportation or by making it possible, through the transfer of energy to the mining sites, to beneficiate the products of the mine locally and ship them to trade centers in the form of refined materials.

3. Nuclear energy will probably make it possible to mine lower grades of material more profitably than we are able to mine at the present time. But Fig. 7 shows how little correlation there has been between input of energy and mineral productivity from 1870 until now.

The application of nuclear energy to mining is usually visualized as involving the fracturing of rock at depth by nuclear explosion, followed by the introduction of leaching solutions or microorganisms to remove the metals and bring them up to the surface. What has to be remembered in this kind of operation, assuming that it can be carried off technologically, is that, first, the rock has to be fractured to the particle size of the metals with which the leaching solutions or microorganisms are to be brought in contact. Second, when leaching solutions or bacteria are introduced, they may be lost to groundwaters, contaminating the subsurface environment. Third, there is the problem of keeping irradiated materials out of the environment and of keeping the product itself from being irradiated so that it cannot be used. Thus a number of

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*End-of-1972 census reports indicate that we are currently doing this *in the United States*—although global populations are still increasing 2% for a 30-year doubling time.

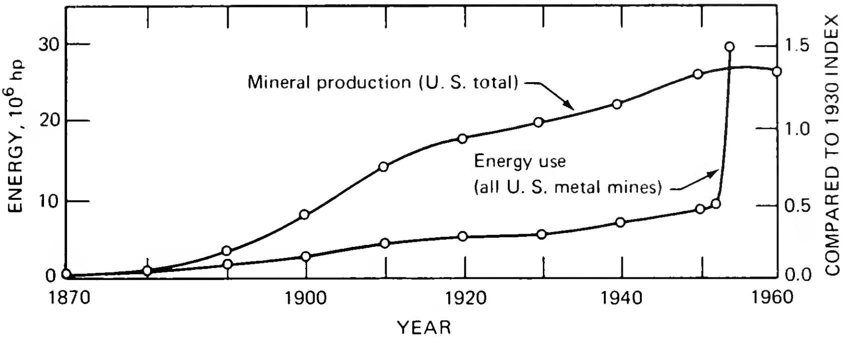

Fig. 7 Energy use compared with mineral production (slightly modified after T. S. Lovering in *Resources and Man*, 1969).

difficulties are involved in the application of nuclear energy to the increase of our resource inventory. Nevertheless, this is an avenue of some promise that ought to be explored to the full with all proper safeguards.

But what about substitution and synthesis? There are, of course, some intrinsic limitations. To begin with, 84 of the 90 naturally occurring elements on the earth already have some commercial use. Second, the synthesis of elements is very difficult to do on the earth. In fact, we know of no metals that can be synthesized except at such temperatures and pressures as prevail in exploding stars, and we have no means of maintaining those pressures and temperatures for times sufficient to create new metal elements here on the earth. Whatever we do in the way of substitution has to be in terms either of substituting common elements for uncommon ones or of substituting new compounds produced through the applications of materials science and technology from common raw materials. Neither of these offers much help with the problem of finding suitable substitutes for things like helium, mercury, gold, germanium, uranium, thorium, tin, and other metals that have unique properties for which there are no satisfactory substitutes and for which the creation of substitutes having such properties is difficult to envisage. A substitute for gold, for instance, which is critical in a number of electronic applications and particularly in the development of high-speed computers, would be very difficult to find. Although we often hear about the substitution of aluminum for copper in transmission lines and some other applications, aluminum is a very unsatisfactory substitute for many of the applications of copper in small machinery and electrical devices. Thus opportunities to relieve pressures through substitution and synthesis are also limited, even though they should be pursued to the limit. Materials science and engineering along with recycling and improved methods of geological exploration are among our main hopes.

As for marine mineral resources, often referred to as a "veritable cornucopia," they are of two main kinds—those which are found as dissolved salts in ocean waters and those which occur in sediments and rocks beneath the ocean floor. The dissolved salts, although vast in quantity, are thinly dispersed and include only 64 of the 84 elements now in commercial use, among them very few metals. Only 15 of these elements are found in quantities of more than 1 lb per million gallons and only 9 of these 15 are found in values of more than $10 per million gallons. Candidly, seawater is more of an arithmetic trap than a horn of plenty.

When it comes to marine resources in sediments and rocks beneath the water column, we again have to think of two main realms. One realm is that of the continental shelves and slopes which belong properly to the continents and which have about the same prospects of resource production as a similar area on the continents, particularly for oil. An increasing portion of our domestic oil resources will come from the continental shelves. The other realm, by far the greater part of the ocean floor, is that of the truly oceanic basins, which are underlain by entirely different kinds of rocks and sediments. These truly oceanic deposits are characterized most importantly by relatively young basic (mafic) volcanic rocks, poor in metalliferous content and moving at rates of a few centimeters per year away from the ocean centers to disappear eventually beneath the continents—the deep ocean floor is everywhere young, limited in variety of metals, and, at most places, sparsely metalliferous. Marine resources, although they may make a few people rich and will certainly produce some useful resources, will not go far toward reducing the main crunch.

Finally, and simply because it comes up so often, I must comment briefly on other planets as abodes for surplus population or for procurement of mineral resources. Is there any validity at all to the view that when Earth becomes too desperately overloaded, we can ship surplus population off to Mars and other planets, or possibly to the moons of Jupiter? Leaving aside the problems of choosing who might go and how living conditions are up there, we have to bear in mind that the present population of the earth is increasing by about 78 million a year, a number equivalent to about 37% of the total population of the United States at the present time. What logistic and financial problems are involved in shipping 78 million or more people a year to other planets? Hardin (1959) calculated that it would take three-fourths of the U. S. annual GNP to ship one day's increase in world population to other planets. The problem of returning raw or refined mineral products from other planets to Earth, assuming they are found, is of comparable dimensions.

It is clear, when we look at the above-mentioned and other limiting factors simultaneously, that the real question is not whether a balance with nature *will* be restored; that it will be is assured by Le Chatelier's principle. The real and pressing question is whether a new and more durable balance with nature will result from thoughtful assessments, decisions, and actions on our part, or whether that balance will come about through harsh but inexorable natural processes over which we have no control. Essential elements in the establishment of balance favorable to ourselves and our descendants include, first and foremost, population control. Whatever else we may do can only be ameliorative and temporary unless populations are stabilized as quickly as possible and eventually reduced to levels preferably not much greater than those now existing. If population levels are only gradually stabilized to about 10 billion near the year 2050, as now seems likely, tough times lie ahead.

The next most important thing after population control is resource and ecosystem management—and, being a geologist, I think of resources as part of the ecosystem. The crux of that problem, as I see it, is how to assure a continuing supply of the basic raw materials to meet the demands of an industrial society that must inevitably continue to grow for some time if the now deprived are to be bettered and how to do so without irreparable damage to the rest of the ecosystem.

A third step that I find essential is to establish some system for the continuing surveillance of all components of a thoroughly researched global ecosystem.

Among many specific recommendations I might make, I will stress here only my conviction that the time has come for mankind to recognize two new fundamental human rights.

1. *First is the right of the fetus not to be conceived or, if conceived, not to be born into a world where its life is likely to be one of misery and privation or where the welfare of its siblings is threatened.* It is time we stopped viewing children as objects to be propagated at the whim of parents who can at least foresee the consequences of their actions and who should therefore have the foresight to limit their reproduction to desired and supportable numbers. To assure that parents are able to do so, society should take appropriate action to assure that no woman will be forced to carry an unwanted child to term. Hardin (1959) has labeled the abortion laws that still prevail over a large part of this country as "compulsory pregnancy," and that seems to be an apt expression of their intent. Those who worry about the right of a fetus to life should not lose sight either of the quality of life that the fetus might enjoy or of the dubious right of anything to live inside the body of another without that other's permission.

2. *Second is the right of society as a whole, through democratic procedures, to determine the size of population that best assures its healthy and stable continuance.* This is a very sticky and difficult problem to be sure, but it needs to be discussed. There has, in fact, been much discussion of a variety of possibly effective coercive measures from the view that such measures will eventually be necessary. There is much, however, that can be done in noncoercive ways that may eliminate or reduce the need to consider coercion. We can repeal the antiabortion laws. We can legalize homosexuality. We can encourage forms of fulfillment for women that do not involve marriage or childbearing. We can rewrite first readers and children's stories to show more happy maiden aunts and bachelors and fewer large families. These and many other subtle things can and should be done to influence reproductive activity toward lower population sizes

without interfering overtly with freedom of choice—indeed, most of the measures I have suggested really increase freedom of choice.

If those two new fundamental human rights could be recognized and implemented by effective measures to restore a real freedom of choice about family and population sizes, here and throughout the world, man would have gone a long way toward solving his problems. In doing so, he would also have added substantial force to the belief that there is indeed intelligent life on Earth.

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CARBON IN THE BIOTA

ROBERT H. WHITTAKER and GENE E. LIKENS
Ecology and Systematics, Cornell University, Ithaca, New York

ABSTRACT

Recent estimates of the net primary production of the biosphere converge on a value of about 160 x 10^9 metric tons (dry matter)/year (73 x 10^9 tons C), with values for land and sea production of 105 and 55 x 10^9 metric tons/year, respectively. Gross primary production should be about twice the net primary production for the biosphere as a whole. The energy equivalent of net primary production for the world is 7.0 x 10^{17} kcal/year, implying an efficiency (of net primary production relative to incident sunlight in the visible range) of 0.25%. Biomass for the world in 1950 is estimated as 1820 x 10^9 metric tons (dry matter) (829 x 10^9 metric tons C) very strongly concentrated [all but 3.9 x 10^9 metric tons (dry matter)] on land and especially in forests. Preliminary estimates suggest that herbivorous animals harvest, per year, 7.2 x 10^9 metric tons (7%) land net production and 20 x 10^9 metric tons (37%) marine net production to support animal dry biomasses of 6.8 x 10^9 metric tons on land and 2.5 x 10^9 metric tons in the sea. Man's harvest from the land (primarily about 9.5 x 10^8 metric tons cereals) continues to increase. World biomass is decreasing, however, particularly by the cutting of old-growth forests; and decrease in world productivity from biosphere toxication must now be expected.

As carbon is central to the chemistry of life, so the carbon chemistry of the biosphere is central to biogeochemistry. In this paper we shall characterize the biosphere, the living film of the earth, in terms of its carbon content and major single function, productivity. For this purpose we summarize the best available estimates of the magnitudes of total organic matter (biomass) in this film and the annual rate at which it is renewed (net productivity). We offer preliminary estimates of animal, as well as plant, productivity and biomass.

Serious questions exist about the adequacy of data for these estimates. The magnitude of the world's productivity and biomass can, however, be estimated in two ways: either by stratifying the biosphere into ecosystem types and estimating mean and total values for each of these or by modeling the effects of environmental factors on production and biomass and integrating the results of the model for the earth's surface. We, as well as others, have used the first approach.[80-82] The second approach was developed for productivity of land vegetation by Lieth.[34]

ESTIMATION OF PLANT PRODUCTION BY ECOSYSTEM TYPES

World estimation by ecosystem types depends on knowledge of the total area of each type. For land communities, ecosystem types are likely to be the formation types of plant geographers, or biome types, but for the seas a different breakdown into open ocean, continental shelves, upwelling and estuarine areas, etc. is appropriate. Obtaining geographic areas of the formation types on land is not simple. Formations, or structural types of vegetation, intergrade continuously; consistent classification is difficult both because of this continuity and because of the diversity of types and lack of correspondence of some of the types between Southern and Northern Hemispheres. However, an inventory of areas of formations was published by Vahl and Humlum;[74] and both Lieth[34] and we have used also planimetering of maps, data of the Food and Agriculture Organization (FAO),[21] and other sources, to obtain the areas shown in the first columns of Tables 1 and 2 (compare also Refs. 25, 40, 66).

Given the areas of ecosystem types, it is next necessary to obtain mean productivities and biomasses of these. A wide range of Western research results, which Lieth summarized[33,34] (see also Refs. 2, 42, 44, 79) and which we compiled since that time, has been supplemented by Rodin and Bazilevich's[57-59] summaries of Russian work. Other sources have been used for marine (Refs. 10, 29, 51, 55, 63, 64, 71, 72) and freshwater (Refs, 35, 56, 77, 78) productivity. There is much disparity in the information available on different ecosystem types; our data for temperate forests are not bad, those for other temperate and arctic communities are reasonable, those for tropical communities are very meager. Both aquatic and terrestrial production measurements are subject to intrinsic difficulties of technique; but systematic sources of error may be more vexing, and the estimates consequently less secure, for aquatic communities than for terrestrial ones. To obtain the means in columns 3 and 7 of Table 1, we have averaged sets of reported values when these seemed adequate, but in other cases (e.g., tropical forests, savanna, desert scrub) the "mean" is a subjectively chosen intermediate value based on very few measurements. Reliability of means is affected also by exceedingly wide dispersions in the values for some ecosystem types (particularly lake and stream, algal bed and reef, and estuarine communities). It is important that values be based on the full range of conditions of an ecosystem type and not only on the high productivities in more favorable conditions.

The estimates of world production and biomass are given in Table 1, columns 4 and 8. The marine production total represents the convergent estimates of our earlier table,[80,82] Ryther,[64] and Koblenz-Mishke, Vokovinsky, and Kabanova,[29] although Riley[55] and Bunt[10] have suggested these estimates

TABLE 1 PRIMARY PRODUCTION AND BIOMASS ESTIMATES FOR THE BIOSPHERE*

1 Ecosystem type	2 Area, 10^6 km^2 = 10^{12} m^2	3 Mean net primary productivity, g C/m^2/year	4 Total net primary production, 10^9 metric tons C/year	5 Combustion value, kcal/g C	6 Net energy fixed, 10^{15} kcal/year	7 Mean plant biomass, kg C/m^2	8 Total plant mass, 10^9 metric tons C
Tropical rain forest	17.0	900	15.3	9.1	139	20	340
Tropical seasonal forest	7.5	675	5.1	9.2	47	16	120
Temperate evergreen forest	5.0	585	2.9	10.6	31	16	80
Temperate deciduous forest	7.0	540	3.8	10.2	39	13.5	95
Boreal forest	12.0	360	4.3	10.6	46	9.0	108
Woodland and shrubland	8.0	270	2.2	10.4	23	2.7	22
Savanna	15.0	315	4.7	8.8	42	1.8	27
Temperate grassland	9.0	225	2.0	8.8	18	0.7	6.3
Tundra and alpine meadow	8.0	65	0.5	10.0	5	0.3	2.4
Desert scrub	18.0	32	0.6	10.0	6	0.3	5.4
Rock, ice, and sand	24.0	1.5	0.04	10.0	0.3	0.01	0.2
Cultivated land	14.0	290	4.1	9.0	37	0.5	7.0
Swamp and marsh	2.0	1125	2.2	9.2	20	6.8	13.6
Lake and stream	2.5	225	0.6	10.0	6	0.01	0.02
Total continental	149	324	48.3	9.5	459	5.55	827
Open ocean	332.0	57	18.9	10.8	204	0.0014	0.46
Upwelling zones	0.4	225	0.1	10.8	1	0.01	0.004
Continental shelf	26.6	162	4.3	10.0	43	0.005	0.13
Algal bed and reef	0.6	900	0.5	10.0	5	0.9	0.54
Estuaries	1.4	810	1.1	9.7	11	0.45	0.63
Total marine	361	69	24.9	10.6	264	0.0049	1.76
Full total	510	144	73.2	9.9	723	1.63	829

*All values in columns 3 to 8 expressed as carbon on the assumption that carbon content approximates dry matter × 0.45.

may be low. The values, first computed as dry matter,[80,82] have been multiplied by 0.45 to obtain the values for C given. These values are net primary production, i.e., the amount of organic matter (or its energetic equivalent) synthesized by photosynthesis of green plants that remains after the respiration by these plants. The total organic matter produced by the plants (exclusive of photorespiration, but before true respiration) is gross primary productivity. The fraction of gross productivity respired by plants apparently ranges from 50 to 75% in many forests (with the higher of these values in the Tropics) downward 20 to 40% in many other terrestrial and aquatic communities.[41] Too few measurements of plant respiration in the field are available to permit effective estimation of gross primary production for the world. In general, however, the higher respiration rates for forests and lower ones for other communities should compensate for one another and give a gross primary production for the world that is approximately twice the net primary production[80] (compare also Ref. 25).

Columns 5 and 6 of Table 1 give mean energy equivalents for organic carbon in plants of the different ecosystem types[34] and energy fixed in net primary productivity. Lieth[34] estimates world net photosynthetic efficiency (energy of net primary production/energy of sunlight at the earth's surface) at 0.13%. This value is convergent with estimates based on less detailed analysis of caloric values—0.25% for net primary production relative to sunlight in the visible range at the earth's surface,[80] and 0.24% for gross primary production relative to the full spectrum.[25] Efficiency of gross primary production for light in the visible spectrum should be about 0.5%. The magnitude of world energy fixation[14] in gross primary production, about 1.4×10^{18} kcal/year, far exceeds man's total use of fossil fuels and other industrial energy, which was about 4.7×10^{16} kcal/year in 1970.

PRODUCTION AND BIOMASS RELATIONS TO ENVIRONMENT

The second approach to production estimation is through quantitative relations to environmental variables. Efforts to deduce the amount of productivity by way of what ought to be possible for the photosynthetic processes are likely to give exaggerated values. The works of Riley,[53] Ryther,[62] and Russell-Hunter[61] are approaches of this sort that seem unrealistic in relation to field measurements. A more reliable approach is that of induction, establishment of the relations of actual production measurements to environmental variables.

For terrestrial communities the principal variables are moisture availability and temperature; additional variables are sunlight intensity, nutrient availability, and seasonal change in climatic factors. A number of people have established correlations of productivity with these variables or combinations of them. Walter[76] showed that in grasslands of fairly dry climates the aboveground production increased with precipitation in a nearly linear manner, at 1 g m^{-2}

year^{-1} per millimeter of precipitation. Paterson[48,49] has employed formulas using several climatic variables (mean temperature of the warmest month, range between warmest and coldest months, precipitation amount, length of growing season, and insolation). Rosenzweig[60] has shown an effective, logarithmic relation between net primary production and actual evapotranspiration: log NAAP = (1.66 ± 0.27) log AE − (1.66 ± 0.07), in which NAAP is net annual aboveground productivity in grams per square meter per year, AE is annual actual evapotranspiration in millimeters, and 5% confidence limits are given. Russian work (Refs. 3, 4, 11, 16) has related production to the ratio of radiation intensity and the amount of heat needed to evaporate the annual precipitation. It is not difficult to establish a variety of such correlations, but none of these has been applied to estimation of world production.

To make possible such estimation, Lieth[34] has simplified the variables to the two that seem most critical and are most widely available in climatic data—mean annual temperature and mean annual precipitation. Production data are plotted in relation to these variables, as shown in Figs. 1 and 2, and curves are fitted to the data. The equations for these curves are then applied to climatic data to give two production estimates for each station; of the two the lower is chosen as the better estimate by the principle of limiting factors. This technique of prediction may not please the physical scientists among you. It is an approach governed by feasibility, using the curves fitted to dispersed data to average out the many factors that affect productivity but cannot be used for the

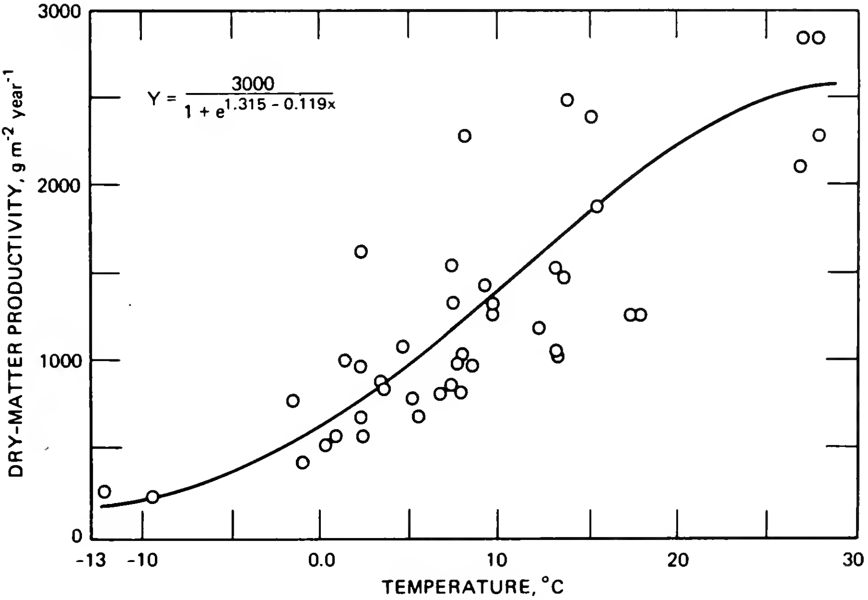


Fig. 1 Annual dry-matter productivity vs. mean annual temperature.[34]

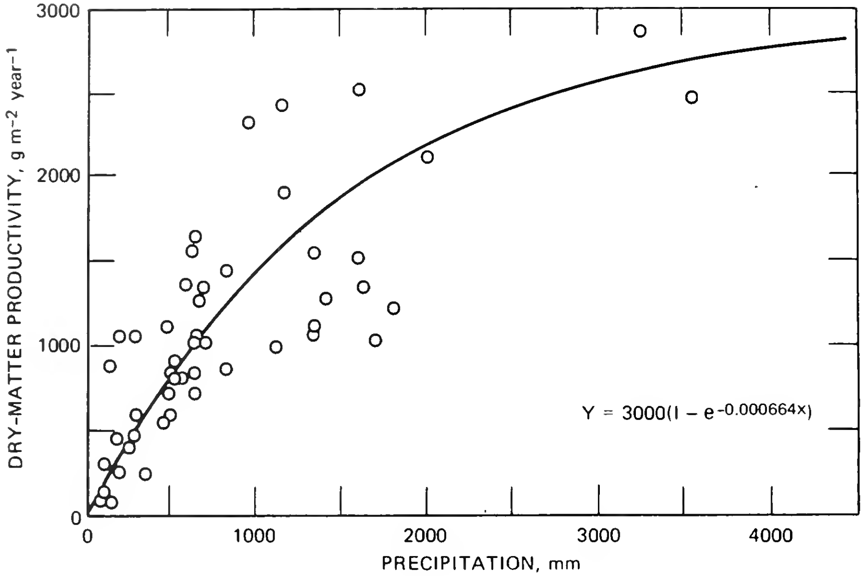


Fig. 2 Annual dry-matter productivity vs. mean annual precipitation.[34]

worldwide prediction. Lieth[34] (compare also Refs. 3–6) has used the technique to prepare a map of net annual primary production of the land surface, shown in Fig. 3. The map implies production values for the land close to those of Table 1; the two approaches should of course largely agree since they use different ways of averaging some of the same production data. Despite the relation of marine production to nutrient levels that Steele,[69] Riley,[54] and others have sought to model, there is no comparable treatment of the oceans.

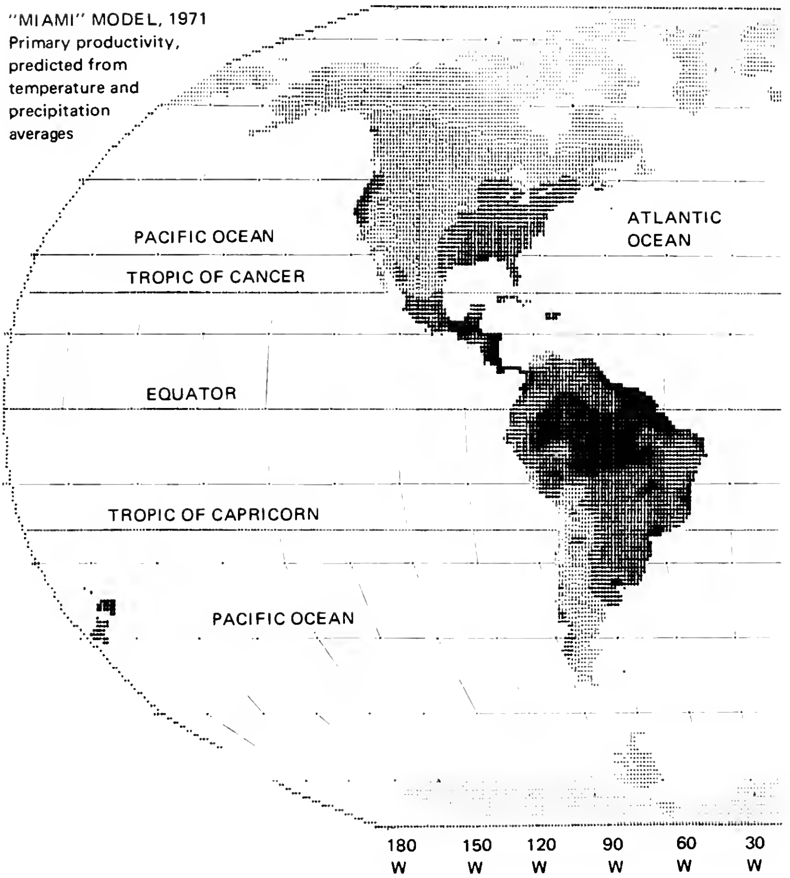
Biomass data are somewhat less amenable to this treatment than are production data. In general, on both land and sea, biomass is correlated with productivity; but these correlations are loose. The relation may be expressed as a biomass-accumulation ratio—the ratio of biomass present in living organisms to net annual primary productivity, both in dry matter or carbon per unit area (Table 1, column 7/column 3). The reciprocal ratio of production to biomass is sometimes used;[37] but this less effectively expresses some of the relations of interest, particularly the correlations of biomass accumulation with size and longevity of dominant organisms, the consequent time scale of community stability, development of community structure and diversity of niche offered small animals, size of nutrient pools in organisms, and extent of environmental modification by the community. The time spent by organic matter in plants varies widely for different tissues, but the biomass-accumulation ratio may be taken as an average "residence time" in years for carbon or organic matter in the plant community. Normal ranges of such biomass-accumulation ratios on land are 1.0 to 3 for many grasslands, 3 to 10 for desert scrub and shrublands, 10 to 30 for woodlands and young forests, and 30 to 50 in mature forests.[79,80] For a given level of productivity, the biomass-accumulation ratio and biomass are strongly affected by the age of a young community, or the mean longevity of the dominants of a mature one. Figure 4 shows the relation for some of our forest data; a comparable plot for grasslands would give a much lower slope, expressing lower biomass-accumulation ratios. Marine and terrestrial communities are different realms of correlation of biomass and production. Whereas on land with vascular plants dominant, biomass-accumulation ratios range from 1 to 50 or more; in plankton communities with their short-lived algae, these ratios are small fractions of 1, probably one-twentieth to one-fiftieth. From this contrast results the biomass disparity of land and sea as shown in Table 1, column 8. Land production may be about twice that of the seas, but land plant biomass appears to be 600 times that of the seas, and more than 1000 times that of all the phytoplankton of the oceans.

HISTORY AND THE RELATIVE PRODUCTIVITY OF LAND AND SEA

Table 2 summarizes estimates of world primary productivity (compare Ref. 34). We think these of interest in two connections: first, the reliability of the estimates, and, second, the relation of land and sea production.

The wide contrasts in early estimates would be expected. Liebig's[32] was a casual estimate of what world production would be if the world's surface were covered by a moderately productive meadow [500 g (dry matter) m^{-2} $year^{-1}$]. He was not too far from current estimates since the weighted mean production of the world is, we think, that of a dry grassland or semidesert (320 g m^{-2} $year^{-1}$). The Ebermayer[17] and Schroeder[67] estimates are based on less happy choices from too-limited data, and these influenced the low estimates of Fogg,[24] Müller,[40] and Lehninger.[31] Early estimates of marine production, based on potential rather than actual production,[53,62] seem much too high. Bowen's[9] estimates use values from an article by Westlake[77] that is, for this purpose, biased by selection toward maximum values. We believe the estimate of Bazilevich, Rodin, and Rozov[6] also was influenced by preference for high values. The remaining recent estimates are those of Whittaker and Likens,[80,81] SCEP,[65] Lieth,[34] Golley,[25] and we suggest the combination of the marine estimate of Koblentz-Mishke et al.[29] with Olson's[47] terrestrial estimate. These five values give an average of 161 × 10^9 metric tons (dry matter)/year with a coefficient of variation of 5.8%. This seems a reasonable convergence and acceptable dispersion, considering the nature of the effort; but it should be noted that Golley[25] used our mean productivity values, and some of the other estimates are not fully independent

A point that has come into focus since the early estimates is the disparity of productivity on land and sea. If temperature and light are largely equivalent for land and sea, and water and nutrients the key determinants of production for



	<0.1	0.1–0.25	0.25–0.5	0.5–1.0	1.0–1.5	1.5–2.0	> 2.0 kg (dry matter) m^{-2} year^{-1}
LEVEL	0	1	2	3	4	5	6
	FREQUENCY DISTRIBUTION OF DATA-POINT VALUES IN EACH LEVEL						
SYMBOLS	░	▒	▤	▥	▦	▩	■
FREQUENCY	59	97	152	262	180	146	105

both, then the land, much of which is desert, might be far less productive than the sea as suggested by Riley.[53] The inference has proved lopsided; for if productivity on much of the land is limited by drought and cold, productivity in much of the sea is limited by nutrient poverty. The critical nutrients, phosphorus and nitrogen, are carried downward by settling organisms and their remains from the lighted, surface waters of the seas. The nutrients are thus depleted in the photosynthetic levels of much of the open ocean. The

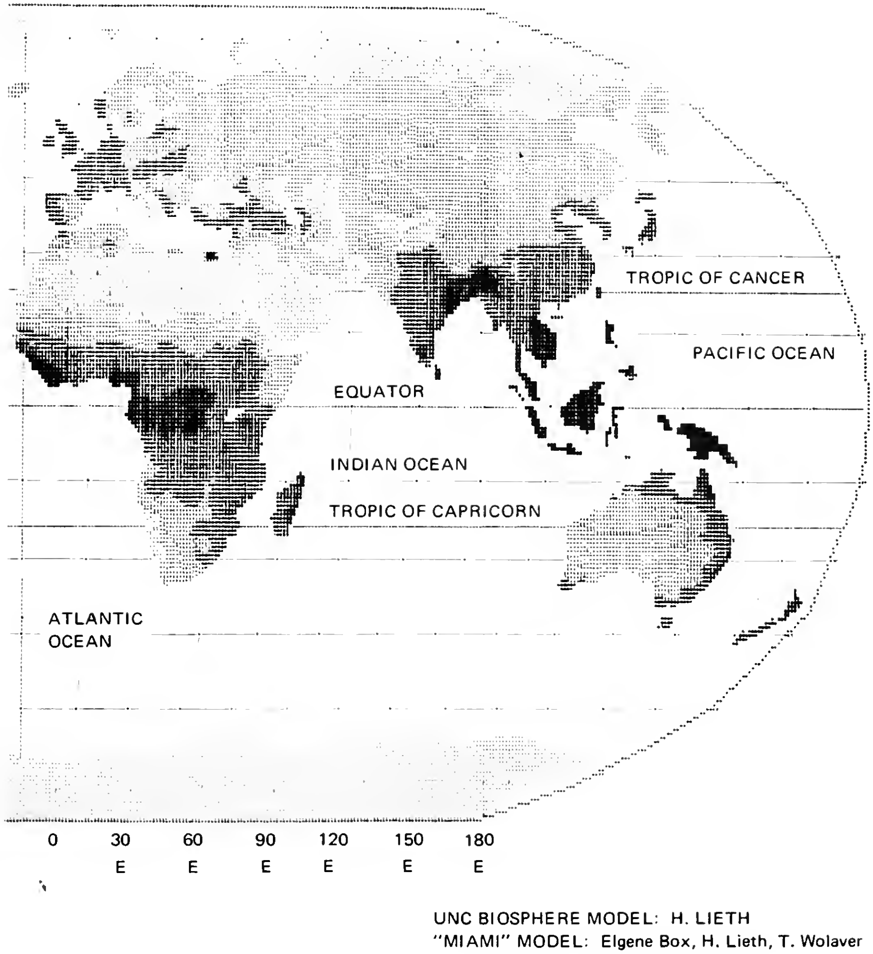


Fig. 3 Productivity of the land surface of the earth, as predicted from the relations shown in Figs. 1 and 2.[34]

productivity supported by the remaining low nutrient levels, and turbulent and other return from deeper waters, is mostly in the range of 20 to 100 g C m^{-2} $year^{-1}$. This range is about one-tenth that of typical, nondesert terrestrial communities. If one asks a key reason why a forest should have a production 10 times that of a plankton community, it may be the same as the reason the forest may have a biomass 10 thousand times that of the phytoplankton: stability of surface. The forest occupies a fixed surface on which it can develop a

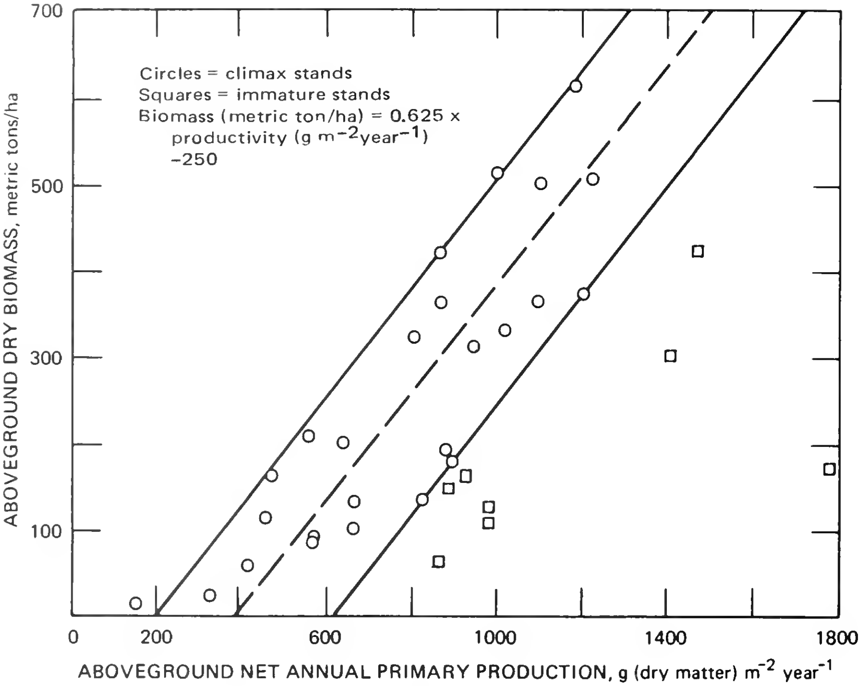


Fig. 4 Biomass vs. productivity in forest samples from the temperate United States; data of Whittaker,[79] Whittaker and Woodwell,[82] and unpublished samples. Samples in the upper part of the oblique band are old-growth climax forests; those in the lower part of the band are climax or near climax, although some are affected by disturbance; those below the band and represented by squares are young and clearly immature forests. The low range of productivity, 200 to 600 g m^{-2} year^{-1}, represents environments marginal for forest growth; the samples in this range are woodlands of small trees in open growth, rather than true forests.

massive structure accumulating nutrients into plant tissue and tending, by partly closed cycles between soil and plant tissue, to hold these nutrients against loss. The short-lived phytoplankton has no such means for the long-term accumulation and conservation of its nutrients. The forest has evolved a degree of biological control of nutrient availability; for the phytoplankton, physical processes such as turbulence more directly govern nutrient availability.

The critical determinants of production are thus moisture, nutrients, and temperature, with very different weightings of these for land and sea. The very highest productivities are in communities combining abundant water with moderate or high temperatures and continuing nutrient replenishment, such as some floodplain forests and salt marshes, coral reefs and kelp forests, certain tropical lakes and rivers, and fertilized rice and sugar cane fields.[35,80] On land

TABLE 2

ESTIMATES OF WORLD PRIMARY PRODUCTIVITY

			Amounts estimated, 10^9 metric tons			
	Date	Form of estimate	Land	Sea	Total	Net dry-matter equivalent, C × 2.2
Liebig[32]	1862	C, net			255	255
Ebermayer[17]	1882	CO_2			90	61
Schroeder[67]	1919	C, net	16.3			
Noddack[43]	1937	C, net	15.1	28.6	43.7	96
Riley[53]	1944	C, gross	20	44 to 203	166	365
Steemann Nielsen[70]	1958	C, net		15		
Fogg[24]	1958	C, gross	24	32	56	123
Ryther[62]	1959	C, net		53		
Müller[40]	1960	C, net	10.3	25	35	77
Deevey[15]	1960	C, net	56.4	33.4	90	200
Vallentyne[75]	1965	C, net	22 to 32	22 to 28	44 to 60	115
Lehninger[31]	1965	C, net	16.6	16.6	33	73
Bowen[9]	1966	C, net	106	29	135	357
Whittaker and Likens[80,81]	1969	DM, net	109	55	164	164
Ryther[64]	1969	C, net		20		
Olson[47]	1970	C, net	54			
Koblentz-Mishke et al.[29]	1970	C, net		23		
Bazilevich et al.[6]	1970	DM, net	173	60	233	233
SCEP[65]	1970	C, net	56	22	78	172
Lieth[34]	1972	DM, net	100	55	155	155
Golley[25]	1972	DM, net	89	55	144	144

any sufficiently favorable combination of moisture, temperature, and nutrients can support a forest; and forests, on about one-tenth of the earth's surface area, include almost half of the production and nine-tenths of the mass of the biosphere. The oceans are, in contrast, relative deserts fringed with more productive waters where, in areas of upwelling and on continental shelves, nutrient availability is enhanced.

HETEROTROPH PRODUCTION AND BIOMASS

In Table 3 we have ventured preliminary estimates of animal consumption, production, and biomass. These columns have been pieced together from frankly unsatisfying data and are intended for early obsolescence as data from the International Biological Programme become available. Column 4 of Table 3 gives

TABLE 3 ANIMAL SECONDARY PRODUCTION AND BIOMASS ESTIMATES FOR THE BIOSPHERE

1 Ecosystem type	2 Area, 10^6 km^2	3 Animal consumption, %	4 Herbivore consumption, 10^6 metric tons C/year	5 Total animal production, 10^6 metric tons C/year	6 Animal biomass, g C/m^2	7 Total animal biomass, 10^6 metric tons C
Tropical rain forest	17.0	7	1100	110	9	150
Tropical seasonal forest	7.5	6	300	30	5.4	40
Temperate evergreen forest	5.0	4	120	12	4.5	22
Temperate deciduous forest	7.0	5	190	19	7	50
Boreal forest	12.0	4	170	17	2.2	26
Woodland and shrubland	8.0	5	110	11	2.2	18
Savanna	15.0	15	700	105	6.8	100
Temperate grassland	9.0	10	200	30	3.1	28
Tundra and alpine meadow	8.0	3	15	1.5	0.2	1.6
Desert scrub	18.0	3	18	2.7	0.2	3.6
Rock, ice, and sand	24.0	2	0.1	0.01	0.0004	0.01
Cultivated land	14.0	1	40	4	0.2	2.8
Swamp and marsh	2.0	8	175	18	4.5	9.0
Lake and stream	2.5	20	120	12	2.2	5.5
Total continental	149	7	3258	372	3.1	457
Open ocean	332.0	40	7600	1140	1.1	360
Upwelling zones	0.4	35	35	5	4.5	1.8
Continental shelf	26.6	30	1300	195	2.7	72
Algal bed and reef	0.6	15	75	11	9	5.4
Estuaries	1.4	15	165	25	6.8	9.5
Total marine	361	37	9175	1376	1.24	449
Full total	510	17	12433	1748	1.78	906

the net primary production that is consumed by herbivorous animals, based on estimates of percentage consumption in different ecosystem types (column 3 of Table 3) applied to total net primary production. Some consumption percentages on land have been compiled by Golley;[25] we have used values ranging from 1% for cultivated land and 2 to 3% for desert and tundra to 4 to 7% for forests and 10 to 15% for grasslands. Higher consumption percentages are reported for grasslands and savannas; we judge these values (25 to 60%) to be too high for a world average of aboveground and belowground consumption in grasslands that mostly lack efficient harvest by African ungulates. For aquatic communities we have used values ranging downward from 40% in the open oceans[55] to 35% in upwelling zones, 30% in continental-shelf waters, and 15% in algal beds and estuaries (with a higher harvest of plankton and lower harvest of vascular plants). Mean estimated consumption percentages are 7% in continental, and 37% in marine communities.

Data on efficiencies of food use by invertebrate animals are limited, and many data on vertebrates are of doubtful applicability to populations under field conditions. Slobodkin[68] gives a range of gross growth efficiency (new protoplasm/food ingested) from 4 to 13% in *Daphnia*; and a net growth efficiency (new protoplasm/food assimilated) of 55 to 59%. Assimilation efficiencies[12,13] (food assimilated/food ingested) for marine zooplankton are widely variable with many of the values between 40 and 80%; gross growth efficiencies must be lower, and for these Riley[55] suggests 16% for marine zooplankton and an uncertain higher value (24%) for benthic animals. For a salt-marsh grasshopper and snail,[19,68] gross efficiencies were 13 and 6%, net efficiencies 37 and 14%. Engelmann[19] obtained a gross efficiency (mortality/ingestion) of 4.2 for oribatid mites. Column 5 (Table 3), animal production, is based on multiplying herbivore consumption (column 4, Table 3) by gross efficiencies of 15% for marine communities, grasslands with their grazing mammals, and desert scrub with its seed eaters, and 10% for all other continental communities. We suspect the result is a high estimate of "net" secondary productivity—increase in carbon-containing mass by growth and reproduction of primary consumers. Productivity of animals on higher trophic levels is based on harvest of part of this secondary productivity and should be of the order of 10% of its amount. Our estimates give the somewhat surprising result that animal secondary production is less than 1% of net primary production on land and 5 to 6% in the sea. The ratios of assimilation or "gross" animal secondary production (growth + reproduction + respiration + organic excretion) to gross primary production should not be widely different from these.

Animal-biomass values for various communities have been compiled as a basis of column 6 (Table 3). Data are available for temperate forests,[18,52,73] a small tropical rain forest[46] and a mangrove swamp,[26] tundra vertebrates,[50,83] and marine communities;[55] and data for the grassland biome were made available to us by J. K. Marshall (personal communication); we have used interpretations and interpolations from these to fill out the column. The biomass estimates given by Kovda[30] seem to us far too high. In most terrestrial communities, animal biomass is concentrated in small and short-lived invertebrates rather than the more conspicuous vertebrates; earthworms are apparently the most massive animal group in forests (Refs. 18, 46, 52, 84). Vertebrate biomass may exceed invertebrate biomass in grasslands supporting populations of large grazing mammals,[36] and Riley[55] suggests that in the sea biomass may be higher in longer lived animals of higher trophic levels than in the zooplankton.

Our estimates suggest that (because of higher consumption percentages in the sea) the contrast in total production between land and sea is reversed, going up the trophic pyramid from producers to primary consumers. About three-quarters of world animal production (excluding man and domestic animals) may be in the sea. Our total animal-biomass estimates are closely similar for the continents and the seas, although animal biomass may be only one two-thousandth of plant biomass on land, but one-quarter of plant biomass in the seas (in which mass of zooplankton at times exceeds that of phytoplankton). Since columns 5 and 7 (Table 3) are estimated from independent sources, the relation between them as affected by size and longevity of animals is potentially of interest. We attach no significance to the ratios of animal biomass to animal production as estimated for particular ecosystem types. The averages of these ratios (1.23 on land, 0.33 in the sea) suggest, however: (1) The predominance in community function of small animals with life-spans of a year or less. On both land and sea the greater part of animal biomass appears to be in smaller and more obscure organisms—zooplankton rather than fish, and arthropods and soil animals rather than birds and mammals. (2) Marine zooplankton have shorter lives and more rapid mass turnover than terrestrial invertebrates. Table 1 does not include production, consumption, and biomass of man and domestic animals. Borgstrom[8] estimated the world biomass of livestock animals as 925×10^6 metric tons liveweight, compared with 180×10^6 metric tons for man himself (in 1960). These values, converted to carbon for the population of 1970, are about 120×10^6 metric tons C in livestock and 23.6×10^6 metric tons C in man.

We have not presumed to estimate reducer or saprobe (bacterial and fungal) production and mass for ecosystem types from the scanty material available. It is reasonable, however, to treat the biosphere as approaching (apart from the effects of man) a steady state of the whole in which total respiration of all heterotrophic organisms essentially equals total net primary production. Given this equality, total reducer assimilation should approximately equal net primary production minus animal assimilation (column 4, in Table 1, minus column 5, in Table 3, and animal respiration). (Complications affecting this relation include use of animal tissues and excreta by reducers, and consumption of dead plant tissues by animals, some of which use as food bacteria and fungi of decay rather than the plant tissues themselves. We have no basis on which to evaluate these complex food-chain relations and the role of mycorrhiza in terrestrial communities.) Growth efficiencies (new protoplasmic carbon/substrate carbon) for reducers on land are probably higher overall than gross growth efficiencies of animals. Growth efficiencies may be in the range of 30 to 40% for fungi of decomposition, 5 to 10% for aerobic bacteria, and 2 to 5% for anaerobic bacteria.[1] If we use 20% as a reasonable intermediate growth efficiency for terrestrial reducers, then total reducer production on land is of the order of 9.4 × 10^9 metric tons C/year and 23 times total animal secondary production. If we assume a growth efficiency of 5 or 10% for marine reducers, then marine reducer production would be 0.7 to 1.4 × 10^9 metric tons C/year, or about half to about the same as our estimated marine animal production. Small size and rapid turnover in bacterial cells and fungal hyphae make possible the massive secondary productivity by these organisms that are obscure to us, and that in the oceans probably have biomass much less than that of animals. It may not be the case that biomass of fungi on land is small compared with that of animals.

EFFECTS OF MAN

We may ask finally what the effects of man's growth in population and power are on world biomass and production. Biomass is reduced when perennial grassland is replaced by annual crops and when grassland and shrubland are, with erosion, degraded to desert-like communities. The greatest reductions of biomass are those involving the greatest fraction of the world's biomass—the forests—whether the reduction is by clearing for agriculture, urban and suburban spread, increased fire frequency, or timber harvest. When old-growth forests are replaced by plantations subject to harvest while still young, the average biomass of the young stands is only a fraction of that of the old. A modification of Table 1 assigning the present agricultural lands to other ecosystem types and giving higher biomass values for climax conditions to the forests suggests that world biomass before the influence of civilized man was over 1000 × 10^9 metric tons C. The values in Table 1 are estimated as of 1950, before more recent, systematic cutting in Amazonia and elsewhere in the tropics and intensive harvest in the Temperate Zone. The rate of harvest of wood products,[20,23] about 5 × 10^8 metric tons C/year, does not indicate the rate of forest clearing. It is difficult to relate our estimates for forest production and biomass to the FAO[20,23] data for gross increment and growing stock in "the world's forests in use" and the FAO's[20] ". . .most serious warning. Changes in world forest resources are slow, and there is in fact insufficient evidence to assert that the present plantation programmes are making serious headway against the destructive pressures exerted on the forest by a fast-growing population." However, the FAO[20] reported a world growing stock of 238 × 10^9 m^3 (including bark) on 55% of the world's forest area in 1960. The carbon equivalent should be roughly 110 × 10^9 metric tons C in all plant parts in reported forests and plantations, a value markedly below our estimate for forests before the effects of man (world biomass of 1000 × 10^9 metric tons C, × 90% for forest biomass, × 55% for corresponding area, is 500 × 10^9 metric tons C).

It appears that world biomass is being effectively reduced as older growth forests are replaced by younger growth and clearings, but we cannot estimate the rate of this process. Probably the amount of carbon being held in organic forms is being reduced also by the reduction in organic content of soils that follows the clearing of natural vegetation.[25] Biogeochemical consequences include not only those on the carbon cycle itself but the more indirect contribution of biomass reduction and erosion to the increased transfer of nutrients from land surfaces to water bodies.

Man's relation to world productivity is, like his relation to nature, ambivalent. Irrigation may increase land production and erosion reduce it; increase in atmospheric carbon dioxide may enhance production whereas that of other pollutants reduces it; fertilization increases land production whereas fertilizers and toxins from the land may reduce useful aquatic production. Only by detailed study, and then with uncertainties, could one assess the balance of these effects and the rate at which the balance is shifting. Increase in productivity of man's crops is, on the whole, slow, difficult, and demanding and at best keeps pace with population growth or falls somewhat behind. The contamination and toxication of the biosphere are, in contrast, accelerating at a rate reflecting the much more rapid growth of technology, as this rapid growth is made possible by fossil fuel and other power sources. The terms of the race imply that the influences toward reduction of productivity should in due course prevail. We are not suggesting that the time is here or that man's food supply—except, perhaps, for the marine fisheries—is now limited by these effects.

Most of the biosphere's net production is not suitable, or not harvestable, for human food. Man harvests (in 1970) about 5.5 × 10^8 metric tons C in cereals and other plant foods,[21,81] somewhat more than one-hundredth of land production, from arable lands now producing somewhat more than one-tenth of land production. Man is now harvesting animals for food to the amounts of about 33 × 10^6 metric tons C/year (including milk and eggs) on land and 7.5 × 10^6 metric tons C/year from water bodies.[21,22,81] These yields are currently increasing at rates larger than that of population growth. The other side of the ambivalence is present only in incipient form, in the known reduction of plant growth by air pollution in major urban areas,[27,39] and suspected effect of acid rain (from pollutant SO_2 and NO_x), discussed by Hill[28] in reducing growth of forests in northwestern Europe and northeastern United States.[7] We suggest that food production on land can still increase for some time but that with continued growth of industry a widespread reduction of biosphere productivity, at present inconspicuous but in the future accelerating, should be expected.

The biosphere is now increasingly vulnerable to widespread, adverse influences of human industry. Industrial society may also be increasingly vulnerable—dependent as it is on economic growth, complex organization, and the unstable psychology of human beings—to detrimental effects on its own environment, health, and resource base. Industrial society is at present committed to accelerating growth, made possible by a variety of positive feedback effects. The character of this growth, combined with the difficulty of decisions in a world of nations, implies that the growth of industrial society may be expected to overshoot the capacity of the biosphere to support man and tolerate his toxins.[38,80,81] From this relation we will only predict increasing effects on the mass and productivity of the biosphere in this decade and refer in passing to the likelihood that the relation between these two vulnerable systems is unstable.

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DISCUSSION BY ATTENDEES

Hall: The 1967 report of the President's Council on World Food Problems strongly suggests that the principal way open to us for increasing world agricultural productivity is through increasing the degree of industrialization, i.e., shift increasingly to a situation in which roughly 1 cal of fossil fuel is needed for each edible calorie. Since you have suggested that continued industrialization would potentially decrease plant productivity, we may be in a serious dilemma—our best way to increase productivity will result, possibly, in a decrease in productivity. Do you agree?

Whittaker: That is just another facet of what I refer to as an unstable relation.

Cloud: Please amplify the reasons for the great discrepancy between biomass and primary production indicated by your data showing land biomass to be 600 times that of the oceans compared to a terrestrial productivity that is only twice that of the oceans.

Whittaker: These are the different realms of the relation between biomass and production on land and sea that I referred to. It results directly from the contrast in size of organisms and longevity and the striking consequent difference in biomass accumulation ratio between land and sea. This is the difference between microscopic organisms with a lifetime of a fraction of a year as opposed to trees with decades.

Colinvaux: Do you have any estimates of the rate at which the Amazon forests are being removed?

Whittaker: I sure would like to know—or would I? I do not have good data on the rate at which forests are being removed. I know only that I do not like what I see.

Welch: What will be the effects of the decrease in world biomass caused by forest harvest?

Whittaker: I would assume that the biomass is going to decrease in other areas, too. When one replaces Southern California chaparral with lawns (which no longer burn up houses), one is reducing biomass. Most of the things that man does reduce biomass; the few exceptions to this would be in a prairie area where a residential neighborhood that is a kind of man-made woodland is created. I think, overall, the direction almost everywhere must be one of decrease in biomass. I cannot really speculate on the overall effect on the carbon cycle.

Mitchell: Recalling Dr. Machta's estimate in the opening session that something of the order of one-quarter of the fossil carbon added to the atmosphere may be going into the biosphere, I just made a quick calculation that this represents only about 0.1% increase per year in the total biota carbon reservoir you estimate in your paper. This would be extremely difficult to measure if we want to verify by actual measurement that this is really where some of the fossil atmospheric carbon is going.

Whittaker: This seems to me almost impossible in terms of method. Under experimental conditions, one can pick up the effect, but in natural communities the difficulties are staggering. A friend in California pointed out to me the possibly happy effects of air pollution in the great valley of California—that air pollution first increases the CO_2 levels and then produces a diffuse canopy that has a ground-glass effect on the light, dispersing it. Both of these, he said, should tend to increase productivity of the farming areas of the Great Valley of California. I though him too sanguine.

Reiners: Am I correct in surmising from your paper that it is unlikely that terrestrial biomass is increasing and thus serving as a carbon receptor for excess fossil-fuel CO_2?

Whittaker: I think that the cutting of forests is the overwhelmingly dominant influence.

Richardson: To what extent might it be possible to estimate world net productivity from seasonal changes in atmospheric CO_2 measured at a number of selected stations around the world? These seasonal changes were dramatically evident in the records from the Mauna Loa observatory which were presented earlier in this symposium.

Whittaker: I have no idea. This seems to be a tenuous kind of extrapolation from such measurements in the few places where they could be made, but all I can say is that it is an interesting idea. I think that no one has tried it.

Deevey: Note that my own independent estimates from Rodin and Basilevich's data yield the opposite conclusion from yours from the same data, i.e., it is at least arguable that the biota is growing and not diminishing. I want to stress that, even if you are right, the vital effect of clearing a tropical forest stand is to *increase*, not decrease, the productivity. Substitution of immature for mature systems will normally have this effect, in the short run of course.

Whittaker: I agree that this is too complex a matter to debate here, but I would observe this: although it is true that individual immature forest stands are growing, at the same time many of these and others are being cut. Considering the manner in which forest cutting is progressing, I myself must believe that it is the cutting which prevails over the growth in the overall average.

Deevey: If the cutting exceeds the growth, one result is to increase, not to decrease, the productivity. Under reasonable treatment of a cleared forest, the substitution of an immature for a mature stand can increase the net annual productivity of the biomass.

Whittaker: There are circumstances in which it is true that the unstable stand has the higher production than the stable and some circumstances in which it is not true.

Woodwell: Could the flux of net primary production into humus balance the loss of standing crop of biota?

Whittaker: It might, but I expect the humus to be in some kind of steady state governed not so much by the biomass of the forest as by the input of foliage and branch litter as opposed to decay rates. I do not think that the reduction of forest biomass could be compensated for by an equivalent increase in litter biomass.

Reiners: Forests grow in most years—there is always a true increment, as Rodin and Basilevich have expressed it, so that biomass increases in a logistic curve. However, harvesting in forests is very often catastrophic even in nonhuman situations, and, although there will always be a true increment, every 200 or 300 years it is all going to go back down again. So, when productivity in forests is measured on a year-by-year basis, forests seem to be continually growing. The impression is misleading unless one takes into account that trees are blown down, burned, or cut.

TERRESTRIAL DETRITUS AND THE CARBON CYCLE

WILLIAM A. REINERS
Department of Biological Sciences, Dartmouth College,
Hanover, New Hampshire

ABSTRACT

The objectives of this paper are to review methods for estimating carbon turnover in terrestrial detritus and to provide an estimate of turnover. Reviewed are the input method, the direct CO_2-evolution-measurement method, and the ^{14}C-isotope method. Four approximations of turnover are presented and are based on input data derived from the literature. These approximations range from 37 to 64 x 10^9 tons C/year. Because of human activities, detritus pools are currently not in steady states and it cannot be assumed that inputs equal outputs. In general, man's activities decrease inputs through harvesting and other manipulations and increase outputs by accelerating decay. Thus global carbon output from this pool may exceed current inputs. Since the range of estimates for inputs probably exceeds cultural effects on outputs, it is premature to attempt an estimate of contemporary outputs. A model is presented, however, that may simulate patterns of change and suggest directions for future investigations.

In most ecosystems a proportion of carbon fixed by plants becomes incorporated in material that dies and persists for a time as detritus. On land, detritus accumulates on and in the soil, forming a reservoir of carbon and other biogenic elements that are gradually mineralized and recycled by a myriad of decomposition processes. An enormous literature exists on the biological details of this process.

Terrestrial detritus—termed forest floor, mulch, matting, humus, etc., depending on custom or the ecosystem—represents a significant compartment in an inventory of global carbon. Bolin[1] estimates this compartment to be 700 X 10^9 tons or 1.8% of nonsedimentary global carbon (Table 1). Delwiche[2] estimates the nitrogen content of this pool to be 760 X 10^9 tons. If we assume an average carbon to nitrogen ratio[3] of 12, this leads to 9120 X 10^9 tons carbon for terrestrial detritus—over 10 times Bolin's estimate. A 10-fold difference suggests that further estimates are necessary.

TABLE 1

ESTIMATED CARBON IN MAJOR COMPARTMENTS OF THE BIOSPHERE*

Compartment	Carbon content, 10^9 metric tons	Percent of total nonsedimentary organic carbon	Percent of total nonsedimentary carbon
Atmosphere	700		1.76
Terrestrial plants	450	10.82	1.13
Terrestrial detritus	700	16.83	1.76
Marine phytoplankton	5	0.12	0.00012
Zooplankton, fish	<5	0.12	0.00012
Marine detritus	3,000	72.12	7.53
Sea surface layers	500		1.25
Sea deep layers	34,500		86.55
Sediments	20,000,000		
Coal and oil	10,000		
Totals	20,049,860	100.01	99.98

*Based on B. Bolin, The Carbon Cycle, *Scientific American*, 223: 124–132 (1970).

Workers have modeled detritus pools as subsystems with inputs (litter) and outputs (decomposition), each coming into balance when the detritus pool reaches a steady-state level dictated by climate, soil, and organic factors.[4,5] Although there are some difficulties in the details of this view,[6,7] it forms the theoretical basis for numerous studies on specific dynamics in a wide variety of ecosystem types.

Output from detritus is principally to the atmosphere as CO_2, where a large fraction may be quickly fixed again by plants.[8] Some carbon is lost to the atmosphere in such other gaseous forms as methane and ethanol, especially from anaerobic sites,[9] and some is lost to groundwater solution via carbonate equilibrium reactions and as soluble organic acids, polyphenols, and various other compounds.[10] Some of this organic carbon, reaching streams via groundwater, overland flow, and erosion, is consumed by aquatic heterotrophs in streams,[11] and the remainder enters marine systems. Dissolved inorganic carbon may be released to the atmosphere when groundwater moves into surface waters, or it may be fixed in various forms and carried to the oceans.

To the extent that man is influencing terrestrial detritus pools through cultivation, fertilization, erosion, fire, and lumbering, he is altering rates of output from this compartment which might have an influence on global carbon balances. The objectives of this paper are to review methods for estimating carbon turnover in the detritus pool and to estimate turnover of terrestrial detritus.

METHODS OF MEASURING TURNOVER OF TERRESTRIAL DETRITUS POOLS

A wide variety of methods has been used to gain estimates of decomposition rates. These methods range from microbiological incubation techniques to measurement of weight loss by tethered leaves in the field. All these approaches are of some value in gaining an understanding of cause and effect relations, but most provide only relative measures of decomposition or are restricted to such limited portions of detritus pools as litter layers or humus. Methods discussed in this section include only those designed to estimate turnover of entire detritus pools under field conditions. These fall into three classes, which may be designated as: (1) the input method, (2) the CO_2-evolution-measurement method, and (3) the ^{14}C-isotope methods.

Input Method

This method is based on the principle that, for detritus pools in steady states, outputs must equal inputs. Therefore a measure of carbon input is equivalent to carbon output, and the ratio of input to average pool size expresses the fractional turnover rate for the pool. The inverse of this ratio expresses the average residence time for carbon.

The input method is dependent on the assumption of a steady-state detritus pool. It would obviously be inappropriate for young secondary successional ecosystems, for even quite old primary successional systems, or for systems undergoing some kind of disturbance such as fertilization or irrigation. On the other hand, the error is likely to be small for detritus pools that are asymptotically approaching steady states since the degree of change in pool size may be less than errors of estimate for carbon inputs.

This method also requires measurement of both aerial and subterranean inputs. Aerial contributions are easy to measure in forests in particular, and a significant volume of data on forest litterfall exists, much of it reviewed up to 1964 by Bray and Gorham.[12] Aerial-litterfall collection is methodologically simple, but it is laborious and requires at least one annual collection cycle. Furthermore, there can be wide differences in year-to-year variation.[12-14] Only a few measurements on the contribution of foliar throughfall and stemflow to detritus have been made,[15] but, while this fraction may be qualitatively important, quantitatively it is probably very minor.

Carbon contribution by underground organs is much more difficult to measure, usually involving indirect methods and broad assumptions. Many of these estimates are based on root biomass measurements from cores or excavation pits. The simplest assumption is that the ratio of root production to root biomass equals the ratio of shoot production to shoot biomass.[16] In some cases, root material is sorted by diameter-size classes and turnover rates based on separate intensive studies applied to these compartmentalized biomass measurements.[17] As in the above-mentioned cases, Kimura[18] assumed that root contribution to detritus equaled root productivity, which was, in turn, simply estimated as one-third that of stems and branches. Woodwell and Marples[19] estimated root contribution indirectly by subtracting aerial inputs from an independent estimate of the A horizon annual decay rate. Kucera et al.[20–22] have conducted relatively detailed investigations on root turnover in a tall-grass prairie. Their method essentially involved measurement of root biomass in soil cores several times over a growing season and subtraction of minimum from maximum values. Although executed very carefully, their method—along with most other methods—could not measure rapid turnover of root organic matter by root-feeding organisms, by root-hair dieback, or by root secretions. Therefore their results are probably underestimates of energy and carbon flow from roots to consumers. From the point of view of detritus-pool dynamics, however, such losses may be more related to grazing pathways than detritus pathways since direct and rapid consumption by heterotrophs is involved. Thus these data may actually be reasonable estimates of the bulk of carbon involved in detritus-pool storage and turnover.

In summary, the method of estimating detritus-pool turnover with measures of carbon inputs is sound for steady-state or near-steady-state systems. Its principal difficulty lies in the inadequacy of methods for procuring root input data.

Direct CO_2-Evolution-Measurement Method

If we can assume that all but insignificant fractions of detrital carbon are lost through the soil–air interface, the prospect of direct measurement of CO_2 evolution is initially an attractive means of estimating detritus-pool turnover. Theoretically, if the controlling environmental factors can be sufficiently understood, an annual output may be estimated with information on rate responses to environmental factors and data on these factors. An analysis of CO_2 gas is usually performed with KOH absorption cups or by infrared gas analysis.

Unfortunately this method is fraught with serious complications. The most minor among these, at least for well-drained soils, are possible losses of other volatile forms of carbon to the atmosphere or losses of dissolved CO_2 or organic substances to groundwater. This may be especially serious in circumneutral or alkaline soils. Witkamp[23] illustrated a second problem—marked diurnal cycles in CO_2 evolution correlating with diurnal temperature changes. In some cases, CO_2-evolution rates were inversely related to air temperature, presumably because of the forced convection of warm soil air upward. Such cycles are discouraging to attempts to relate CO_2 evolution to soil or air temperatures and to attempts to estimate rates with short-term measurements.

An even more serious question arises from the possibility that, in such deep detritus pools as northern forest floors or grassland soils, these CO_2 measurements are controlled by physical processes and are only indirectly related to biological rates of decomposition. Carbon dioxide is produced chiefly by biological respiration and enriches soil air in CO_2 at the expense of oxygen. Although most respiration occurs near the surface, the CO_2 content of soil air generally increases with depth. Baver[24] reviewed some of the older literature showing CO_2 concentrations in soil air as high as 15%, with considerable variation with depth and season. Soil air exchanges with surface air at rates controlled by diffusion, soil-temperature changes, barometric variations, wind action, and pore displacement and gas transport by percolating rainwater.[24] Of these factors, Baver felt that diffusion was the most important and the others were minor.

If the high potential air volume of soil (average porosity = 50%) and CO_2 contents[24] of up to 15% are considered, it is clear that soil has an enormous storage capacity for CO_2. If diffusion is the principal agency controlling CO_2 flux upward and across the soil–air interface, then CO_2 diffusion will be responsive to concentration, temperature, and pressure gradients, and possibly to surface ventilation.[23,25-27] Only when CO_2 diffusion is in balance with CO_2 production by respiration will CO_2 evolution measure metabolic activity of the soil. Considering the CO_2 storage volume of soils and the complex influences on diffusion, a balance between CO_2 production and CO_2 diffusion out of the soil may be transitory and fortuitous. At the very least, it is mandatory that methods of measuring CO_2 evolution do not influence normal diffusion processes in soils. It is doubtful whether most of the apparatus described in the literature meets this requirement.[25] This fundamental problem is probably of greatest concern when deep detritus pools are involved; such systems as tropical forests may have extremely active, shallow forest floors in which diffusion is less important than ventilation. It is also possible that surface-layer metabolism (a fast process) is so much more productive of CO_2 than deeper layer diffusion (a slow process) that measurements of CO_2 evolution are mainly controlled by actual CO_2 production near the surface.

Inasmuch as CO_2 evolution measures total carbon coming from the detritus pools and soil, it must include contributions from root respiration and metabolism of mycorrhizal fungi. Harley[28] reviewed estimates of mycorrhizal respiration which led him to doubt that measurements of "soil respiration" would be as useful in estimating decomposition processes as commonly thought. Certainly root respiration alone presents a highly significant addition to soil CO_2 content, and compartmental separation of root respiration from decomposition metabolism is a difficult but necessary task. A few workers are attempting such compartmentalization,[22,29] but such attempts require rather broad assumptions or suffer from unavoidable alteration of in situ conditions which may cause serious errors.[28]

In spite of these problems, data from the more thorough field studies utilizing this method make much biological sense. Predictable correlations have been found in the field between temperature, moisture, bacterial density, and age of litter.[22,30–32] Direct measurement of CO_2 output is of unquestionable value in illuminating responses to environmental and biotic factors, but because of methodological problems and confounding contributions by roots and mycorrhiza, data published to date probably reflect relative rather than absolute rates.

^{14}C-Isotope Methods

Jenkinson has written excellent reviews on the application of ^{14}C for soil-organic-matter studies.[6,33] Some of these techniques are proving exceedingly valuable for research on humus chemistry,[34] but only techniques applicable to estimation of total soil-organic-matter turnover will be outlined here.

The first application involves labeling plant material and following changes in activities of detritus fractions over long periods of time. Although this method is extremely useful in analyzing certain soil dynamics, its use for providing estimates for a broad range of turnover rates would be limited by (1) difficulties in uniformly labeling plant materials in such ecosystems as forests and (2) administrative improbabilities in following through a wide range of experiments over long periods of time. Such experiments would be feasible in such short-statured vegetation types as grasslands[35] and at governmental or other institutional field stations.

The second application lies in dating organic matter in soil profiles by the ^{14}C method. If systems are near steady state, carbon age represents mean residence time or turnover time. A number of such analyses have been made on humus horizons which have indicated rather high ages in the range of hundreds to 3000 years.[6,36–38] Carbon-14 dating is inaccurate for periods less than 200 years owing to the half-life of 5730 years and to additions of old carbon to the atmosphere by fossil-fuel combustion.[6] Carbon dating will therefore be most useful for measuring turnover of refractory portions of detritus—especially humus, which is the major carbon reservoir in most soils. On the other hand, humus represents a small fraction of carbon turnover in terrestrial detritus pools. Kononova[39] estimated that about one-third of detritus becomes humified; the remaining two-thirds is completely mineralized rather rapidly. Jenkinson[33] reviewed a series of experiments on decomposition of labeled plant residues in bare-field soils. At the end of 1 year, 68 to 73% of the carbon was lost in 12 tests; after 2 years, 70 to 79% was lost in 11 tests; and after 5 years, 79 to 85% was lost in 8 tests. Thus ^{14}C dating is helpful but in itself inadequate for estimating total detritus turnover.

The third ^{14}C method is based on ^{14}C enrichment in recent organic material due to nuclear explosions. In effect, testing has given a ^{14}C label to detritus around the world.[36] As Jenkinson[6] has pointed out, dating by this method is most precise in the period below 200 years where natural-^{14}C-dating methods are least reliable. This method basically requires an integrated measurement of specific activity of total detritus entering the pool over a period of time, plus a measure of the change in specific activity of the detritus. The ratio of ^{14}C input to increase in ^{14}C activity of the detritus pool is an estimate of turnover time. Operationally, measurement of changes in specific activity in the detritus pool would be just as difficult as the measurement of the mass of carbon input itself, especially root input as described under the input method. In addition, several other assumptions must be met: (1) soil organic matter must be uniformly subject to decomposition, (2) recycling cannot occur, (3) steady-state conditions must hold, and (4) addition and decomposition rates cannot change.[6] In spite of these restrictions, this technique may be useful in certain cases, and it is important that long-range experiments be initiated on a wide range of ecosystem types as soon as possible.

ESTIMATION OF DETRITUS-POOL TURNOVER

Even if difficulties inherent in direct CO_2-evolution-measurement and ^{14}C-isotope methods were resolved, extensive data for a wide range of ecosystems are not available. The following estimates of detritus-pool turnover are therefore based on litter-input data from the literature and, initially, on the assumption of steady states of detritus pools for most of the world.

The First Approximation

The first approximation is based on estimates of world annual net production for ecosystem types[40] together with my own rough estimates of the percentage of production that enters detritus pathways (Table 2).

The rationales for percentages are based on the few measures of energy flow in these systems. They should be evaluated with the consideration that primary production in terrestrial systems is usually estimated by the harvest method—a method based on changes in biomass which rarely takes into account cropping between measurements. Thus much of the energy loss to grazing has already been subtracted.

The swamp and marsh category unfortunately combines wetland forests and herbaceous graminoid systems. It is generally believed that only about 5% of primary production is lost to grazers in steady-state forests,[41,42] and, in fact, grazing losses are apparently low in marshes as well (about 8% in a *Spartina* marsh[43]). However, some production is lost to the detritus pool through export to marine systems from coastal marshes and to fires in inland marshes, so that

TABLE 2

A FIRST APPROXIMATION OF CARBON TURNOVER IN TERRESTRIAL DETRITUS*

Ecosystem type	World net production (dry weight), 10^9 tons/year	Percent of production to detritus	World detritus (dry weight), 10^9 tons/year	Carbon, 10^9 tons/year
Swamp and marsh	4.0	90	3.6	1.8
Tropical forest	40.0	95	38.0	19.0
Temperate forest	23.4	95	22.2	11.1
Boreal forest	9.6	97	9.3	4.6
Woodland and shrubland	4.2	80	3.4	1.7
Savanna	10.5	60	6.3	3.2
Temperate grassland	4.5	50	2.2	1.1
Tundra and alpine	1.1	95	1.0	0.5
Desert scrub	1.3	95	1.2	0.6
Extreme desert	0.07	97	0.1	0.03
Agricultural land	9.1	50	4.6	2.3
Totals	107.8		91.9	45.9

*Based on Whittaker and Likens' estimates of world net primary production[40] and my own estimates of the percentages of net production which enter detritus pools in ecosystem types.

my weighted value for energy flow to detritus pools for this combined group is 90%.

The percentages for tropical, temperate, and boreal forests are for steady-state systems in which there is no further biomass increment. In young forests this percentage is much lower (52% in 40- to 50-year pine–oak and oak–maple stands).[42,44]

The 80% estimate for detritus in woodlands and shrublands is based on the assumption of higher browsing levels plus periodic losses to fire. In savannas, fire may take all grass shoots and tree leaves every year,[45] or grazing may be severe.[46] Grazing and fires are also regular processes in temperate grasslands. Kucera and Kirkham[22] stated that the principal source of detritus to the soil in their tall-grass prairie study area was the root system. Although the shoots might decay on the surface as mulch, apparently fire was a regular removal factor. Actually, grazing may be the most serious of these two factors today because much of the areas that were most frequently burned is now under cultivation and the remainder is heavily utilized for domestic animals.

Considerable variation doubtless exists between types of tundra with regard to energy-flow pathways. Grazing may be periodically heavy in some types of tundra,[47] but it is difficult to know if this is generally true. The value of 95% may be too high, but, since the worldwide production by these types is so low, the error makes little difference in the total estimate. The 95% estimate for desert scrub is based on the Chew and Chew[48] estimate of 2% loss to small mammals in *Larrea* desert and on my assumption that insects and large mammals graze a further 3%.

The estimate of 50% loss to detritus for agricultural land may be too high. A more rigorous estimate could be developed by a careful review of distribution of production in crop plants and the degrees to which roots and stems, as well as fruits, are utilized.

The Second Approximation

The second approximation results from Whittaker and Likens' estimates of biomass[40] in major ecosystem types together with averages of Rodin and Bazilevich's[49] estimates of total detritus ("litter") as percentages of biomass (Table 3). The number of examples on which these averages were calculated

TABLE 3

A SECOND APPROXIMATION OF CARBON TURNOVER IN TERRESTRIAL DETRITUS*

Ecosystem type	Area, 10^8 ha	Mean biomass, tons/ha	Mean annual litter, % of biomass	Mean litter, tons ha^{-1} $year^{-1}$	World turnover, (dry weight), 10^9 tons	World turnover (carbon), 10^9 tons
Swamp and marsh	2	120	36†	43.2	8.6	4.3
Tropical forest	20	450	5‡	22.5	45.0	22.5
Temperate forest	18	300	3.4	10.2	18.4	9.2
Boreal forest	12	200	2.2§	4.4	5.3	2.6
Woodland and shrubland	7	60	35	21.0	14.7	7.4
Savanna	15	40	27	10.8	16.2	8.1
Temperate grassland	9	15	41	6.2	5.6	2.8
Tundra and alpine	8	6	10	0.6	0.5	0.2
Desert scrub	18	7	49	3.4	6.1	3.1
Extreme desert	24	0.2	100	0.2	0.5	0.2
Agricultural land	14	10	50¶	5.0	7.0	3.5
Totals	147				127.9	63.9

*Based on estimates of world net biomass[40] and on estimates of detritus input as percentages of biomass in ecosystem types by Rodin and Bazilevich.[49] Carbon has been assumed to equal one-half of dry weight.

†Average of Rodin and Bazilevich's grass tugai (70%) and a *Thuja* swamp (3%).[44]

‡Average for tropical forests, Table 53 of Ref. 49.

§Average for numbers 7 to 14, Table 9 of Ref. 49.

¶Author's estimate.

varies between types. A better understanding of which examples were used can be found in the footnotes of Table 5. The total turnover estimate of 46 X 10^9 tons C/year derived from primary-production considerations was considered appropriate for maximum input conditions, but the total estimate by this second method is even higher (64 X 10^9 tons). The source of difference between the two results lies in nonforest types and is due, in part, to the inclusion, in the Rodin and Bazilevich data, of grass and shrub shoots in litter of grassland, savanna, and shrubland. This is not an error from their point of view, but, to the extent that fire and grazing remove surface mulch, the litter does not enter the detritus pool in the sense used in this paper.

The Third Approximation

Because of the similarity in data base, it is not surprising that the total estimate for the third approximation (62 X 10^9 tons) is quite similar to that of the second (64 X 10^9 tons). In this case, total-litter measurements in single stands or a few stands, which were presented as typical values by Rodin and Bazilevich, were multiplied by Whittaker and Likens' estimate of areal cover (Table 4). This method is graced by the judgment of Rodin and Bazilevich with regard to representativeness of the data. They may have arranged their stands in different categories, however. Again, there is no allowance for intense grazing or fire in nonforest types.

The Fourth Approximation

This approximation is developed on a larger literature base than the Russian work and rests on a number of assumptions regarding root contributions to litter (Table 5). Where available, ecosystems of all stages of development are included, and, for forests in particular, this estimate probably best represents current conditions. The estimate for total carbon turnover, 37.5 X 10^9 tons, is the lowest of all four approximations. This method suffers, as do all the others, from lack of proper weighting for litter values to area coverage within the type. Much information is lost by the use of simple arithmetic averages that might be exploited by a finer grained division of ecosystem types within the broad categories. For example, the $\frac{1}{14}$ weights applied to the extremely high values for *Arundo donax* and grass tugai are probably out of proportion to their actual areal extent.

Possible errors in estimates for tropical forests are especially serious because of their high areas and high input rates. The average given may be too low for unexploited forests because timberfall, which may equal litterfall,[50] was not estimated in many of the examples. On the other hand, it may approach a proper compensation for current logging and slash-and-burn agricultural effects.

Very productive grasslands are probably overweighted in comparison with extensive but less productive dry steppes more common today. The level of error

TABLE 4

A THIRD APPROXIMATION OF CARBON TURNOVER IN TERRESTRIAL DETRITUS*

Ecosystem type (Whittaker[40])	Area, 10^8 ha	Ecosystem type (Rodin and Bazilevich[49])	Total litter (dry weight), metric tons/ha	World turnover (dry weight), 10^9 tons	World turnover (carbon), 10^9 tons
Swamp and marsh	2	Grass tugai	76.5	15.3	7.6
Tropical forest	20	Subtropical deciduous	21.0		
		Tropical rain forest	25.0		
		Average	23.0	46.0	23.0
Temperate forest	18	Beech	13.0		
		High oak	9.0		
		Artificial pine	5.4		
		Average	9.1	16.4	8.2
Boreal forest	12	Northern taiga pine	3.3		
		Southern taiga pine	4.7		
		Northern taiga spruce	3.5		
		Central taiga spruce	5.0		
		Southern taiga spruce	5.5		
		Birch forests	7.0		
		Forest sphagnum bog	2.5		
		Average	4.0	4.8	2.4
Woodland and shrubland	7	Black Saxual	10.3	7.2	3.6
Savanna	15	Savanna	11.5		
		Dry savanna	7.2		
		Average	9.3	14.0	7.0
Temperate grassland	9	Meadow steppe	13.7		
		Moderately dry steppe	11.2		
		Arid steppe	4.2		
		Solonetzic steppe	11.9		
		Solonetzic arid steppe	3.5		
		Average	8.9	8.0	4.0
Tundra and alpine	8	Arctic tundra	1.0		
		Shrub tundra	2.4		
		Average	1.7	1.4	0.7

(Continued)

TABLE 4 (Continued)

Ecosystem type (Whittaker[40])	Area, 10^8 ha	Ecosystem type (Rodin and Bazilevich[49])	Total litter (dry weight), metric tons/ha	World turnover (dry weight), 10^9 tons	World turnover (carbon), 10^9 tons
Desert scrub	18	Semishrub desert	1.2		
		Semishrub desert with annuals	9.4		
		Subtropical annuals and semishrub	2.4		
		Desert solonchak vegetation	0.6		
		Average	3.4	6.1	3.0
Extreme desert	24	Subtropical lichen and semishrub	0.5		
		Takyr alga communities	0.1		
		Average	0.3	0.7	0.4
Agricultural land	14	6.5 tons/ha production† × 0.5	3.3	4.6	2.3
Totals	147			124.5	62.2

*Based on Whittaker and Likens' estimates of land area occupied by ecosystem types,[40] plus averages of total detritus input by representative ecosystems tabulated by Rodin and Bazilevich.[49] Carbon has been assumed to be one-half of litter dry weight.

†Production value from Whittaker and Likens.[40] The 50% detritus value is author's own estimate.

may also be high for savannas in which there are only two examples and a large area of land surface.

Comparison of Detritus-Input Estimates

All four approximations represent different aspects of flux through terrestrial detritus pools. The first represents carbon input that will be released to the atmosphere by decomposition in a world without man. This total is 85% of Whittaker and Likens' estimate of annual terrestrial primary production.[40]

The second and third approximations represent total carbon return from plants minus some respiratory losses through grazing from principally steady-state systems. Both totals exceed Whittaker and Likens' estimate[40] of terrestrial production (64 and 62 vs. 54 X 10^9 tons C/year).

The fourth approximation most closely represents carbon input that will be returned to the atmosphere by decomposition alone under current conditions of land use. This input is 69% of Whittaker and Likens' primary production estimate.[40]

TABLE 5

A FOURTH APPROXIMATION OF CARBON TURNOVER IN TERRESTRIAL DETRITUS[a]

Ecosystem	Location	Ref.	Detritus input, metric tons ha^{-1} $year^{-1}$ Aerial	Below-ground	Total	Total carbon turnover, 10^9 tons
			Swamp and Marsh (2×10^8 ha)			
Typha, slow stream	Idaho, U. S. A.	56	17.1	7.3[b]	24.4	
Typha, lake margin	Minnesota, U. S. A.	57	14.4	6.6[c]	21.0	
Typha	Minnesota, U. S. A.	57	16.8	7.4[c]	24.2	
Typha	Esthwaite, England	58	10.7	4.6[b]	15.3	
Typha	Oklahoma, U. S. A.	59	15.3	6.5[b]	21.8	
Phragmites, tugai	Amu-Dar'ya, USSR	49 (Table 44)	10.1	7.9	18.0	
Grass tugai	USSR	49 (Table 53)			76.5	
Spartina salt marsh	Georgia, U. S. A.	43	20.0	10.0[b]	30.0	
Arundo donax	Thailand	45			51.9	
Phalaris arundinacea	Esthwaite, England	58	8.7	3.7[b]	12.4	
Salix, floodplain	Quebec, Canada	13	4.8	0.5[d]	5.3	
Maturing floodplain forest	Quebec, Canada	13	6.8	0.8[d]	7.6	
Thuja swamp	Minnesota, U. S. A.	60	5.0	0.5[d]	5.5	
Fraxinus carr	Minnesota, U. S. A.	60	4.4	0.5[d]	4.9	
Nonweighted averages			11.2	4.7	22.8	2.3
			Tropical Forest (20×10^8 ha)			
18 equatorial forests[f]	±10° latitude	12	11.0	1.2[h]	12.2	
5 tropical forests	India	61	3.9	0.4[h]	4.3	
5 tropical forests	India	62	8.6	1.0[h]	9.6	

(Continued)

TABLE 5 (Continued)

Ecosystem	Location	Ref.	Detritus input, metric tons ha^{-1} $year^{-1}$ Aerial	Belowground	Total	Total carbon turnover, 10^9 tons
Eucalyptus	Australia	63	6.8	0.8[h]	7.6	
2 *Mora excelsa*	Trinidad	64	6.9	0.8[h]	7.7	
Rain forest	Thailand	65	23.2	2.6[h]	25.8	
3 rain forests	Congo	49 Table 46	13.9	1.5	15.4	
Rain forest	Ghana	50	21.7[e]	2.6	24.3	
Rain forest	Puerto Rico	66	11.6[e]	2.1	13.7	
Weighted averages[g]			10.2	1.2	11.4	11.4
Temperate Forest (18 x 10^8 ha)						
39 warm temperate	30 to 40° N & S latitudes	12	5.5	0.9[i]	6.5	
163 cool temperate	37 to 62° N & S latitudes	12	3.5	0.6[i]	4.1	
11 deciduous forests	USSR	49 Table 32	5.7	0.9	6.6	
Pinus nigra	Arnhem, Netherlands	7	2.0	0.4	2.4[j]	
Pinus sylvestris	Arnhem, Netherlands	7	2.3	0.3	2.6[j]	
Quercus	Arnhem, Netherlands	7	4.0	2.0	6.0[j]	
Pine–oak	New York, U. S. A.	19	3.4	3.1	6.5	
Quercus ellipsoidalis	Minnesota, U. S. A.	60	4.7	0.8[i]	5.5	
Weighted averages[g]			4.0	0.7	4.7	4.2
Boreal Forest (12 x 10^8 ha)						
6 arctic-alpine forests	37 to 67°N latitude	12	1.0	1.0[k]	2.0	
11 spruce forests	USSR	49 Table 13	2.0	2.0	4.0	
Abies subalpine	Japan	18	9.1	1.7	10.8	
Picea mariana	Newfoundland, Canada	67	2.5	2.5[k]	5.0	

TABLE 5 (Continued)

			Detritus input, metric tons ha^{-1} $years^{-1}$			Total carbon turnover, 10^9 tons
Ecosystem	Location	Ref.	Aerial	Below-ground	Total	
Abies balsamea	Newfoundland, Canada	67	2.9	2.9^k	5.8	
Pinus sylvestris bog	Siberia, USSR	49 Table 9	2.4	0.1	2.5	
Pinus sylvestris bog	Vologda, USSR	49 Table 9	2.4	0.1	2.5	
Hypnum moss bog	Siberia, USSR	49 Table 9	2.9	0.3	3.2	
Weighted averages			2.2	1.5	3.7	2.2
		Woodland and Shrubland (7×10^8 ha)				
8 desert woodlands	USSR	49 Table 44^l	2.4	4.4	6.8	
Calluna heath	Dorset, England	68, 69	1.0	2.8^m	3.8	
Calluna heath	Dorset, England	68, 69	2.9	8.3^m	11.2	
Calluna heath	Dorset, England	68, 69	3.2	9.1^m	12.3	
Ulex europaeus	Taita, N. Z.	70	8.9	2.0^m	10.9	
Weighted averages			2.9	4.8	7.7	2.7
		Savanna (15×10^8 ha)				
Dry savanna	Rajastan, India	49 Table 46	3.2	4.0	7.2	
Mixed savanna	Thailand	45	2.4	0.7	3.1	
Averages			2.8	2.3	5.2	3.9
		Temperate Grassland (9×10^8 ha)				
14 steppe systems	USSR	49 Table 42	2.6	5.1	7.7	
Tall-grass prairie	Illinois, U. S. A.	71	4.4^n	6.1	10.5	
Tall-grass prairie	Illinois, U. S. A.	71	9.1^n	7.0	16.1	
Tall-grass prairie	Missouri, U. S. A.	21	4.5^n	5.4	9.9	
Weighted averages			3.2	5.3	8.5	3.8

(Continued)

TABLE 5 (Continued)

			Detritus input, metric tons ha^{-1} $years^{-1}$			Total carbon turnover,
Ecosystem	Location	Ref.	Aerial	Below-ground	Total	10^9 tons
			Tundra and Alpine (8×10^8 ha)			
Arctic tundra	Composite	49 Table 6	0.3	0.7	1.0	
Shrub tundra	Composite	49 Table 6	0.9	1.4	2.3	
Forest tundra	Composite	49 Table 6	4.4	0.9	5.3	
Dry-grass alpine	Washington, U. S. A.	72	1.1^n	3.2	4.3	
Mesic grass alpine	Washington, U. S. A.	72	2.4^n	7.5	10.0	
Arctic tundra	Alaska, U. S. A.	73	0.8^n	1.0	1.8	
Averages			1.6	2.4	4.1	1.6
			Desert Scrub (18×10^8 ha)			
9 desert systems	USSR and Syria	49 Table 44^o	1.6	2.7	4.3	
Bromus tectorum	Washington, U. S. A.	74	1.0	1.0^p	2.0	
Chrysothamnus viscidiflorus	Idaho, U. S. A.	57	0.5	0.5^p	1.0	
Stipa–Artemisia	Idaho, U. S. A.	57	0.8	0.8^p	1.6	
Artemisia–Stipa	Idaho, U. S. A.	57	1.0	1.0^p	2.0	
Stipa–Poa–Artemisia	Idaho, U. S. A.	57	1.2	1.2^p	2.4	
Larrea tridentata	Arizona, U. S. A.	75	1.3	0.1	1.4	
Weighted averages			1.3	1.9	3.3	3.0
			Extreme Desert, Rock and Ice (24×10^8 ha)			
Sparse desert annuals	Kopet-Dag, USSR	49 Table 44	0.01	0.1	0.1	
Takyr algae	USSR	49 Table 54	0.1		0.1	
Averages			0.05	0.5	0.1	0.1

TABLE 5 (Continued)

Ecosystem	Location	Ref.	Detritus input, metric tons ha^{-1} $year^{-1}$ Aerial	Belowground	Total	Total carbon turnover, 10^9 tons
	Agricultural Land (14×10^8 ha)					
6.5 tons/ha average production x 0.5		40			3.3[q]	2.3
Total carbon turnover						37.5

[a] Based on Whittaker and Liken's estimates of land area occupied by ecosystem types,[40] plus selected data on detritus input from the literature. Necessary assumptions underlying some of the estimates are given. Carbon has been assumed to equal one-half detritus dry weight.

[b] Belowground contribution is assumed to equal 30% of total.

[c] Belowground contribution is assumed to equal 25% of biomass yielding ~30% of total.

[d] Belowground contribution of wetland forest is assumed to equal 10% of total.

[e] Includes timberfall.

[f] Averages of numbers of stands given.

[g] Weighted by numbers of stands comprising original averages.

[h] Belowground contribution is assumed to be 10% of total (see Ref. 49, Table 46).

[i] Belowground contribution is assumed to be 14% of total (derived from 11 stands in Ref. 49, Table 32).

[j] Original data in terms of carbon; doubled for estimate of dry weight.

[k] Belowground contribution is assumed to be 50% of total (derived from 11 spruce stands in Ref. 49, Table 13).

[l] The eight examples chosen are numbers 12 through 20, excepting No. 18.

[m] Belowground contribution was estimated in proportion to root biomass (74% of total in *Calluna* in Ref. 69). This was apparently the basis of computation for Russian woodlands cited above.

[n] Assuming 100% of maximum shoot standing crop goes to detritus as with the Russian data.

[o] The nine examples chosen were numbers 1 through 9.

[p] Root growth is assumed to be 50% of total, and 100% of shoot growth is assumed to become detritus.

[q] Same estimate as in Table 2.

Two estimates from the literature can be compared with these approximations. Plass[51] prepared a partial carbon budget for the world, in which he estimated that photosynthesis and respiration plus decay balanced at 60×10^9 tons of CO_2. It is unclear if his photosynthesis has been corrected for plant respiration, but assuming it has, the respiration of all heterotrophs is 16.4×10^9 tons C/year. If this is added to his estimate of loss of stored carbon from cultivated lands, carbon flux from total respiration is only 17×10^9 tons C/year.

Bolin[1] estimated a flux of 25×10^9 tons C/year through the terrestrial detritus pool. Both of these estimates are lower than the four approximations developed in this paper, but, since neither author explains the basis for his estimate, it is impossible to evaluate these discrepancies.

INFLUENCES OF CULTURAL ACTIVITIES ON TERRESTRIAL DETRITUS TURNOVER

Human activities vary between ecosystem types, but, in general, they tend to divert primary production from detritus pools to human uses and to accelerate decomposition of stored detritus. Whenever harvesting occurs—through haying marshes, cutting timber, grazing savannas and grasslands, or increasing the frequency of burning in forests, shrublands, or grasslands—organic matter is diverted from the organic processes of decomposition. None of these effects influences the carbon cycle in the long term; carbon is ultimately returned to the atmosphere as CO_2 through combustion, respiration of domestic animals, or the rotting and burning of lumber. These effects do decrease carbon input into detritus pools, however, and, in the long run, will decrease pool sizes and net output from these pools to the atmosphere.

The effects of forest harvesting are somewhat ambiguous. Tree-bole removal substantially decreases carbon return to the soil. Where periodic cutting is practiced, the proportion of net primary production flowing to detritus is decreased roughly one-half. On the other hand, there is some evidence that litterfall, excluding timberfall, is higher in younger than in older stands.[49] Nevertheless, it is doubtful that higher litterfall compensates for loss of tree boles, so that the net effect of forestry is to reduce pool size and carbon turnover.

At the same time that cultural activities divert inputs from detritus pools, they tend to accelerate decomposition of stored carbon. The most obvious of these is conversion of forest land and grassland to cultivation. Such surficial detritus as the L and F layers of forest floors and the mulch of grasslands is rapidly eliminated, and the more refractory humus is slowly decomposed to new, lower steady states with slow turnover rates. Rates of decline of the order of 50% in nitrogen content of agricultural soils have been described.[52–54] Since soil nitrogen is largely organic, it is reasonable to assume that carbon decreases in parallel with nitrogen. Plass[51] estimated that such agricultural activity increased carbon release from soils 0.5×10^9 tons C/year above that fixed by photosynthesis. Humus-decomposition rates are very likely higher under these circumstances than would be estimated from ^{14}C-dating methods on undisturbed soils because of the mechanical mixing and enhanced aeration caused by cultivation itself and by the introduction of inorganic fertilizers that may stimulate the microflora. In contrast to cultivation effects, land converted to well-managed pasture may actually accumulate organic matter.[54]

Decomposition of stored organic carbon is accelerated in other ways. Opening of forests tends to raise the temperature of the forest floor, leading to an enhanced microbial respiration. Even the creation of higher frequency of drying–wetting cycles caused by canopy removal may accelerate decomposition.[55]

Other influences leading to accelerated decomposition are draining and cultivation of swamps and marshes, fertilization and microclimatic influences of ground fires, and erosion of soil organic matter from the land to aquatic systems.

In summary, cultural practices invalidate steady-state assumptions, the most important of which is that output equals input. How they change outputs is problematical. Fundamentally, they tend to decrease carbon input into detritus pools and to accelerate losses. In the short run, these effects tend to balance each other out and minimize influences on the rate of carbon flux to the atmosphere. In the long run, however, they will lead to a lower rate of flux.

Because these influences are so varied, it would be an enormous task to assess their current effects for the world—assuming sufficient data are available. Such an assessment is beyond the limits of this paper. Furthermore, effects of cultural practices probably are less than the range of estimates for carbon turnover in detritus for steady-state systems given here. It would be premature to produce a reasonable figure for cultural effects on carbon output when the range of estimates on steady-state systems is still so broad.

The best that might be accomplished at this point is to describe a pattern of change that may be presently occurring, using reasonable but subjectively derived figures. Equation 1 describes a widely accepted model for general detritus-pool dynamics:[5,6]

$$\frac{dX}{dt} = A - LX \tag{1}$$

where X is pool size, A is annual input, and L is the fraction of X decomposed each year. At steady state

$$\frac{dX}{dt} = 0 \qquad \text{and} \qquad \frac{A}{L} = X_e \tag{2}$$

where X_e is the steady state of the pool. To describe the pattern of changes in contemporary detritus pools, I have assumed that the world pool behaves as a homogeneous unit or that these figures represent average rates. I have set initial detritus input rates at 46×10^9 tons and modeled a decrease in rate in proportion to human-population growth to a lower limit of 20×10^9. Decay rate (L) was initially set at 4.6%/year and was modeled to increase in proportion to human-population growth to an upper limit of 10.0%/year. Human effects somehow influence both these processes; a direct proportionality to population seemed to be the simplest possible assumption. Human population follows historical records from 1500 to 1965, after which it continues to grow at the

1965 rate until it reaches a limit of 10 X 10^9 people. This in no way is meant to be a prediction for population. It simply terminates the model.

Detritus-pool dynamics were computed according to this model by a difference-equation procedure iterated every year until all parameters reached limits dictated by the model. I wish to emphasize that Fig. 1 is not meant to represent reality in a quantitative sense but only to portray some essential features of pool dynamics and a possible pattern of change in this compartment of the carbon cycle. We do not know the rates of change in either litterfall or decay and can only guess at possible limits on input and output since these will be products of a future, unpredictable civilization. It is a testimony to our present state of knowledge of the carbon cycle that, of all the parameters in the model, only initial detritus-pool size and litter input are based on data and that, among these, pool-size estimates range from 700 to 9000 X 10^9 tons/year.

Clearly, better measurements of pools and processes are required to construct a realistic model for the carbon cycle.

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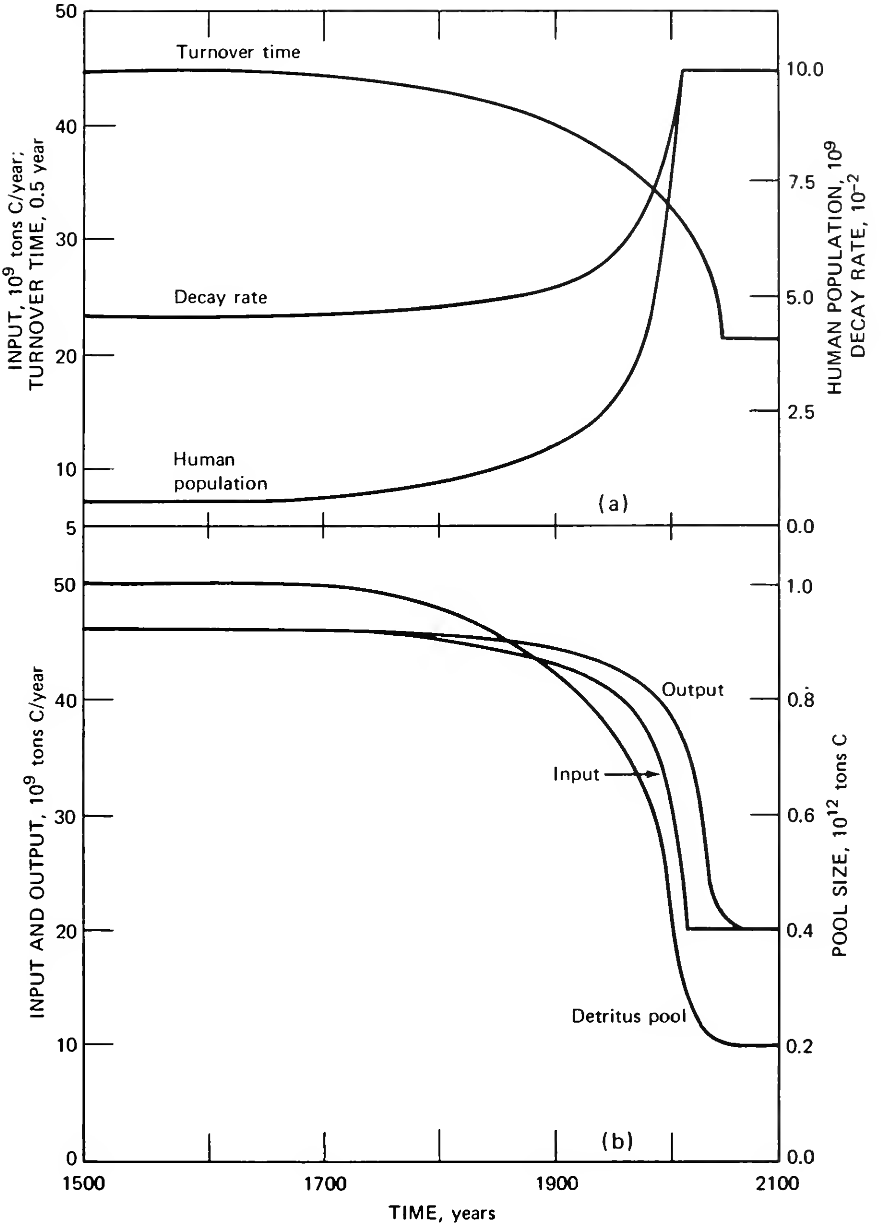

Fig. 1 (a) Human-population increase up to a limit of 10 billion with proportional increase in decay rate of detritus pools; turnover time is calculated as pool size/input. (b) Change in detritus input in proportion to human-population increase; change in output is calculated as a product of decay rate and pool size; change in detritus-pool size is calculated as the difference between input and output.

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DISCUSSION BY ATTENDEES

Livingstone: One cannot safely assume that the ratio of wood pulp to lumber will be much higher in rich countries than in poor ones. The per capita consumption of lumber goes up very rapidly with national wealth, although there are some spectacular deviations from the general trend. Canada, for example, uses more wood than its general standard of living would lead one to expect.

Richardson: As a comment tempering the suggestion that wood use increases rapidly as a nation becomes richer, I would point out that wood is the poor man's fuel, and as a nation becomes richer its wood consumption diminishes. For a majority of the world's countries, the chief use for wood at present *is* as fuel.

Ekdahl: The question is: how does lumber, as a diversion from detritus, compare with paper pulp as a diversion from detritus in terms of volume or weight production?

Reiners: I really do not have a good idea of what the relative proportions might be. My initial guess would be 50–50, at least for Europe and the United States, but, for the world as a whole, I should think that the amount going into pulp would decline relative to lumber.

Allen: This question applies to the previous paper also. What percentage of forest production is currently going into building material, and what is the turnover time of the carbon in this pool? This diversion of carbon from natural detritus pools could be considered a "detritus" pool itself.

Reiners: I do not have the answer. We are diverting lumber from normal detritus pools to another kind of detritus pool which, I would guess, is turning over more slowly.

Olson: We are getting closer to the question of whether man can or will have an effect. I take it that there is already an answer, even if the real coefficients are somewhat different from those you used. I wonder if you have some projections on what should be done next in inquiring into the sorts of human decisions and questions of policy that are involved in these methods.

Reiners: I guess I am rather conservative in saying what is next. I really would like to see a better integration of knowledge and better data before I would personally be willing to play a role in saying something political about this. I am hesitant to say how serious all these things are until we get better information than we have now.

Olson: That does not seem very conservative—to do nothing when the situation is changing very rapidly is not a conservative thing to do.

ESTIMATING THE EFFECTS OF CARBON FERTILIZATION ON FOREST COMPOSITION BY ECOSYSTEM SIMULATION

DANIEL B. BOTKIN,* JAMES F. JANAK,† and JAMES R. WALLIS†
*School of Forestry, Yale University, New Haven, Connecticut, and
†IBM Thomas J. Watson Research Center, Yorktown Heights, New York

ABSTRACT

We have used a computer model of a forest ecosystem to investigate the effects of carbon dioxide fertilization on the structure and function of that ecosystem. Simulated fertilization was carried out, assuming only that an increase in CO_2 increased the annual diameter increments of all trees by an equal percentage. The model predicts that this treatment would weight the environment in favor of shade-tolerant, long-lived species and hasten the process of succession. Changes in productivity and biomass would be obscured by these effects and by the stochastic processes of mortality and seedling survival.

That individual green plants grow better in air enriched with carbon dioxide has been known since the 18th century. The effects of such an enrichment of earth's entire atmosphere on natural terrestrial ecosystems are hard to foresee. Meager knowledge of ecosystems and their innate complexity makes difficult an assessment of the long-term ecological effects of any environmental perturbation, but even if knowledge were plentiful, our minds would have difficulty assessing the probable outcome of any complex mechanism, such as an ecosystem, that operates overtime with many feedback loops. What one needs is a tool that faithfully remembers the implications of one's assumptions and faultlessly moves the system through time. It is obvious that computer modeling and Monte Carlo simulation could provide such a tool, but so far few successful ecological applications have been reported. Why is this? Have we been victimized by inappropriate theories? Have we made the wrong hierarchical assumptions? Have we insisted on accurate micro components and hoped that these would automatically interface to give reasonable macro simulations? Probably all have their own themes for the dearth of successful ecosystem simulations, but most will agree that the power of the computer has yet to be realized in ecology.

We have recently reported elsewhere a computer simulation that successfully reproduces the population dynamics of trees in a forest. The simulation has a basis that makes it an appropriate tool for considering the effects of various perturbations on natural communities (Botkin, Janak, and Wallis, 1972a and 1972b). This simulation was constructed with a biological orientation, reflecting currently available information and assumptions about terrestrial communities. We tried to create a model that would be dynamic in the sense that changes in its state would be the result of its current state plus random components. In such a model the cumulative effects of perturbations are not necessarily obvious beforehand nor analytically predictable from the initial conditions.

We make no claims that this simulation provides a definitive treatment of a forest ecosystem. We claim only that it is a reasonable approximation of current understanding of the population dynamics of forest tree species and that it successfully reproduces the general dynamic characteristics of a forest. Here we shall use the simulation in an attempt to assess: what carbon dioxide fertilization of a forest would do to the structure and function of that ecosystem; how much fertilization would be necessary to produce significant changes; and what these changes would imply for the global cycle of carbon. After the fact, our results appear somewhat obvious, but we present them here because we believe that they do show up some interesting deficiencies in knowledge.

Before considering our simulated experiments, we believe that it is necessary to understand the basis of the model, of which a brief description follows. For a more complete discussion of the assumptions and limitations of the model, the reader is referred to Botkin, Janak, and Wallis (1972a).

DESCRIPTION OF THE MODEL

The simulation was originally designed for use in the Hubbard Brook Ecosystem Study in the White Mountains of New Hampshire. In its present version it simulates forests typical of that study area and of northern New England. However the underlying concepts are general, and in theory the simulation could be extended to many terrestrial ecosystems.

In the simulation, tree species* are defined by a few general characteristics: a maximum age, maximum diameter, and maximum height; a relationship between

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*Sugar maple (*Acer saccharum*), beech (*Fagus grandifolia*), yellow birch (*Betula alleghaniensis*), white ash (*Fraxinus americana*), mountain maple (*Acer spicatum*), striped maple (*Acer pensylvanicum*), pin cherry (*Prunus pensylvanica*), chokecherry (*Prunus virginiana*), balsam fir (*Abies balsamea*), red spruce (*Picea rubens*), white birch (*Betula papyrifera*), mountain ash (*Sorbus americana*), and red maple (*Acer rubrum*) (nomenclature follows Gleason, 1968).

height and diameter, between total leaf weight and diameter, between rate of photosynthesis and available light, and between relative growth and a measure of climate; a range of soil-moisture conditions within which the species can grow; and the number of saplings that can enter the stand under shaded, open, or very open conditions. The abiotic environment is defined by elevation, soil depth, soil moisture-holding capacity, percentage of rock in the soil, a set of average monthly temperatures and precipitation records from a nearby weather station, and by a value for the annual insolation above the forest canopy.

Direct competition among individuals is restricted to competition for light (taller trees shade smaller ones, and species with more leaves for a given diameter shade smaller competitors more than other species; under shaded conditions, photosynthesis is higher for shade-tolerant species than intolerant ones, and vice versa). Species strategy is also invoked by species-specific survival probabilities and by differential addition of new saplings in relation to light at the forest floor. Because the annual probability of survival of an individual is related to the maximum known lifetime of its species, individuals of long-lived species have a better chance of survival in any one year than those with short maximum lives.

Two basic kinds of species strategies are defined in the simulation, those of shade-intolerant and shade-tolerant trees. The former strategy is to capitalize on catastrophe, to provide many young individuals soon after a clearing occurs in a forest, to grow quickly when the light intensity is high, and to produce viable seeds in a comparatively short time. This strategy is to get in and get out quickly and to sacrifice durability and individual persistence for speed. The shade-tolerant strategy is characterized by the ability to grow at all ages in comparatively deep shade, to live a long time, but to grow slowly even when light conditions are high. This strategy sacrifices productivity for persistence and capitalizes on the older stages of a forest. Species with this strategy are characteristic of the climax stage of a forest. There are intermediate strategies, of course, such as that of yellow birch, but the dichotomy is drawn here to help clarify the reader's understanding of the simulation.

The program is written entirely in FORTRAN IV, using only standard library routines and a good uniform random-number generator. A complete listing of the source deck is available from the authors, and a flow chart for the main program, called JABOWA, is given in Fig. 1. The program has been successfully operated under the IBM time-sharing system (TSS) release 7, the Cambridge Monitor System (CMS), and in batch modes. Prospective users with similar facilities should have no trouble using the simulator.

For each plot year of simulation, three major subroutines are called: subroutine GROW, which deterministically provides the annual growth increment for each tree; subroutine BIRTH, which stochastically adds new saplings; and subroutine KILL, which stochastically decides which trees die. Certain features of the simulator are the result of constraints imposed by its initial application to the Hubbard Brook Ecosystem Study.

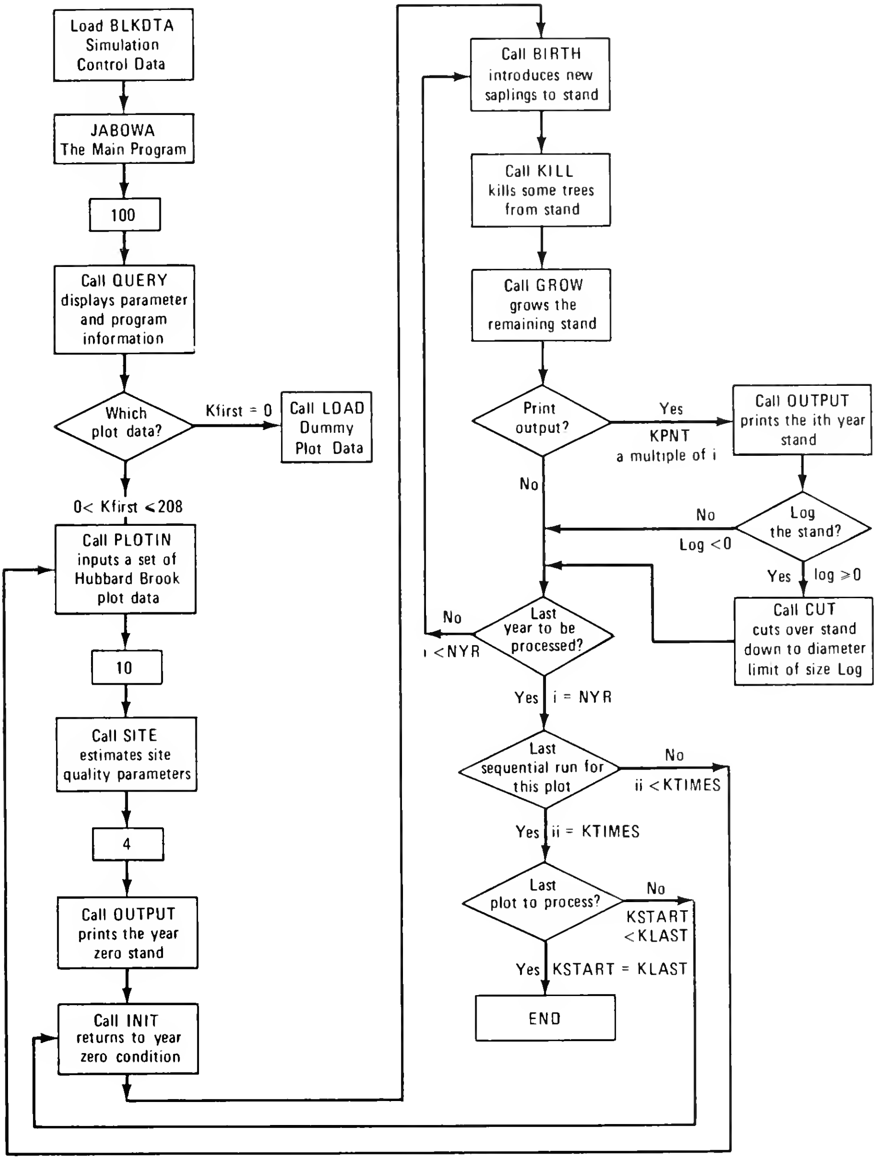


Fig. 1 Flow chart of JABOWA, Version 1 [D. B. Botkin, J. F. Janak, and J. R. Wallis, Rationale, Limitations, and Assumptions of a Northeastern Forest Growth Simulator, *IBM Journal of Research and Development*, 16(2): 101–116 (1972)].

THE EXPERIMENTS

Although CO_2 enrichment of photosynthesis has been known for a long time, at this writing no quantitative descriptions exist concerning the effect of an increase in CO_2 concentration on the growth of any of the tree species found in the Hubbard Brook forest. This forest includes 13 tree species and is typical of forests found above 500 m in northern New England. This forest and its general type have been described elsewhere, and only those features pertinent to our subject are presented here (Bormann et al., 1970; Braun, 1950). Suppose, lacking information about effects of CO_2, we make the simple assumption that an increase in CO_2 concentration would increase the annual growth increment of each tree in a forest by an equal percentage. One can then ask how great an increase would be necessary to produce a significant change in the forest vegetation, and what kind of changes would occur.

At first glance these questions seem simple and the answers obvious: an increase of k percent in the growth of each tree each year would increase the growth of the entire forest k percent. Second, at any time the standing crop of the fertilized forest would be k percent greater than the normal forest. A further deduction seems equally obvious and has been made public by leading scientists quite recently: any increase in the atmospheric concentration of CO_2 will result in an increased growth of vegetation, an equal fractional increase in storage of carbon in the biota, and therefore vegetation will serve to buffer the atmosphere against such changes in CO_2 concentration.

To some the answers may seem so simple and obvious as to demand no further consideration. We have found to the contrary that applying this simple initial treatment to our simulation leads to different but entirely reasonable conclusions. These suggest that to accept the previously mentioned simplistic conclusions at face value is to ignore the complex interactions that occur among species in a natural ecosystem.

Our simulated experiments are merely to compute the normal growth of each tree each year, on the basis of the state of the forest in that year, and then to increase its growth by a constant percentage. Thus ΔD, the annual diameter increment of any tree, is

$$\Delta D = \Delta D' \times k \qquad (1)$$

where $\Delta D'$ is the diameter increment computed normally, and k is the assumed percent increase due to the fertilization effect of carbon dioxide.

Suppose this treatment were carried out on a forest that had just undergone clear-cutting and was beginning secondary succession. How would its development compare to a similar just cutover forest under "normal" conditions? For our experiments we chose an elevation of 762 m in northern New Hampshire. This is a transition zone between conifer forests, typical of higher elevations and more northerly latitudes, and hardwood forests, typical of lower elevations and

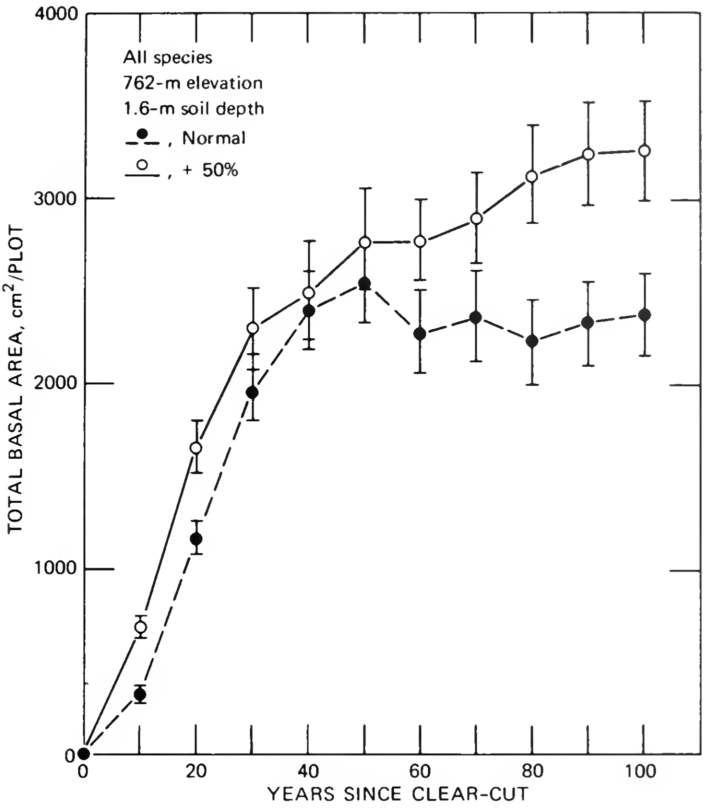


Fig. 2 Simulated change in total basal area per 10- by 10-m plot during the first 100 years of succession following clear-cutting for forest stands whose trees had normal and 50% greater than normal annual diameter increments. Shown are the mean and 95% confidence intervals for 100 replicates in each treatment.

more southerly latitudes. One expects this elevation to be a sensitive zone for a New England forest. Since none of the species is at its optimum, any environmental change might have a strong effect on any species, and perturbations might produce more pronounced effects here than elsewhere.

Experiments were carried out at four levels of treatment: 10, 20, 50, and 100% increase in annual individual tree growth. The predicted effect on total basal area for 50% increase during the first 100 years of secondary succession is shown in Fig. 2. Although the total basal area of the treated forest is significantly greater than the normal forest during the first and second and later decades, there is no significant difference for the third, fourth, and fifth decades. At the end of 100 years, the ratio of the treated to normal means is 1.4 : 1.0; however, with 95% confidence this ratio could be anywhere between 1.15 : 1.0

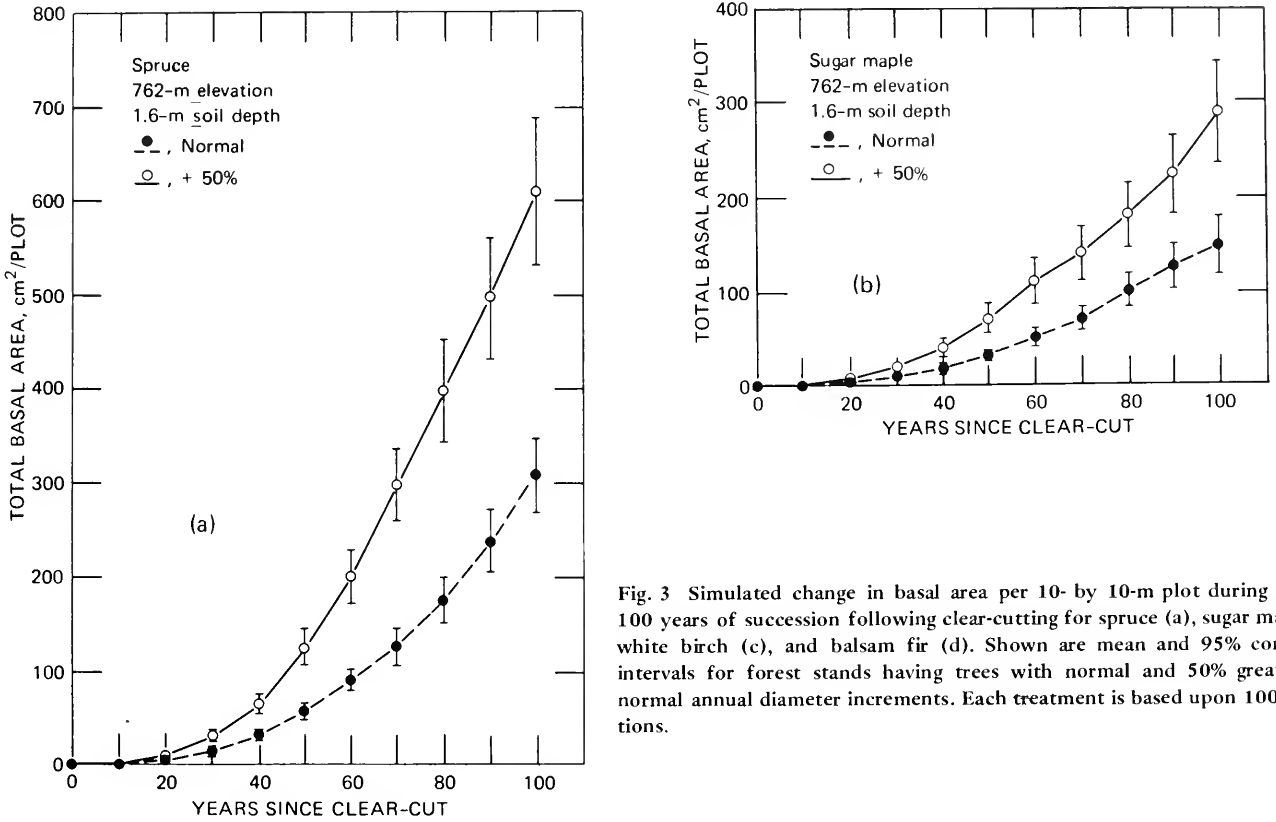
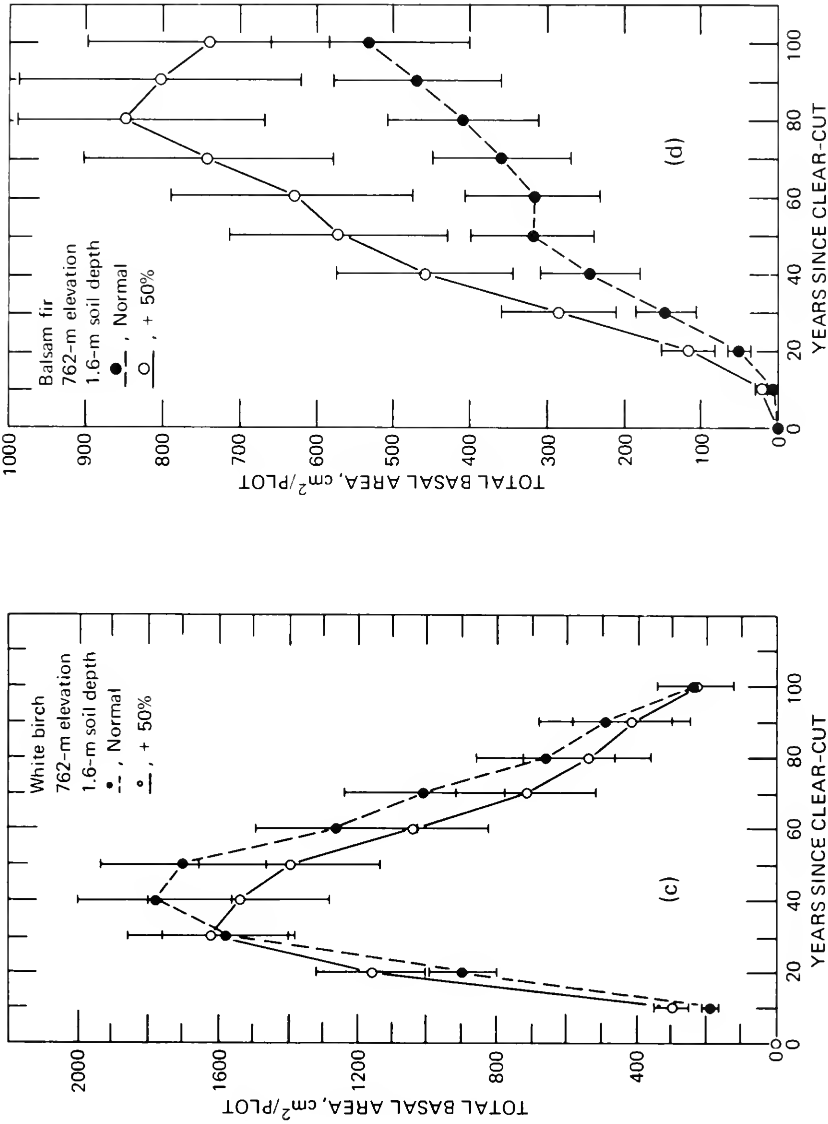


Fig. 3 Simulated change in basal area per 10- by 10-m plot during the first 100 years of succession following clear-cutting for spruce (a), sugar maple (b), white birch (c), and balsam fir (d). Shown are mean and 95% confidence intervals for forest stands having trees with normal and 50% greater than normal annual diameter increments. Each treatment is based upon 100 replications.


Balsam fir
762-m elevation
1.6-m soil depth
●, Normal
○, + 50%
(d)
TOTAL BASAL AREA, cm²/PLOT
0
100
200
300
400
500
600
700
800
900
1000
YEARS SINCE CLEAR-CUT
0
20
40
60
80
100
White birch
762-m elevation
1.6-m soil depth
•, Normal
∘, + 50%
(c)
TOTAL BASAL AREA, cm²/PLOT
0
400
800
1200
1600
2000
YEARS SINCE CLEAR-CUT
0
20
40
60
80
100

and 1.64 : 1.0. The predicted effect of the fertilization is much less obvious than one would have expected from a simple linear extrapolation.

A naturalist hiking through the two forests would for much of the period have a hard time distinguishing the treated from the normal on the basis of appearance. Although this result may at first seem surprising, with a little reflection it seems quite reasonable. There are three factors that account for it: First, the model assumes that birth and death in a natural forest are noisy, and this tends to obscure some seemingly drastic treatments.

Second, the fertilization affects the importance of the different species in the stand. Species characterized by the shade-tolerant strategy, such as spruce [Fig. 3(a)] or sugar maple [Fig. 3(b)], show greatly increased growth during the first century; by year 100 the basal area of each is approximately twice that in the control forest.

The effect of the fertilization on the growth of white birch, which is characterized by the shade-intolerant strategy, is considerably different [Fig. 3(c)]. Although this species does slightly better in the first decade, its basal area thereafter is not significantly different from its basal area in the control forest, and after year 30 the mean value is lower in the treated than in the untreated forest.

The explanation for this is clear. Under the fertilization the shade-tolerant species do so much better that they become stronger competitors against the white birch. Spruce and sugar maple grow taller and develop more leaves faster than normal, and their resultant ability to suppress white birch at least cancels out the fertilization effect on the birch.

The third effect is shown in the growth of balsam fir [Fig. 3(d)]. This species is shade tolerant, but has a lifetime that is short compared to spruce and sugar maple. Although it does significantly better in the first 90 years, its importance in the fertilized forest seems to be decreasing in the last 2 decades, and its average basal area is not significantly different from the control in year 100. The fertilization appears to suppress the time scale for the balsam fir, so that its peak basal area is reached sooner, but its final importance appears to be unchanged.

Similar experiments carried out with 10 and 20% treatments suggest that, in general, the treated forests are not distinguishable from normal ones, either in average total basal area or the average basal area of individual species.

Long-term characteristics of the simulated forests are shown in Figs. 4 and 5 for a more extreme treatment, an increase of 100% in the annual diameter growth of each tree. In this case the long-term average total basal area is significantly different for the treated forest, but the difference is in a ratio of approximately 1.5 to 1.0 for the means. The treated forest reaches a peak basal area slightly earlier than the control, suggesting again that one effect of the fertilization is to compress the time scale.

The behavior of individual species is similar to that of the 50% increase (Fig. 5). During the first century spruce and sugar maple do much better, white

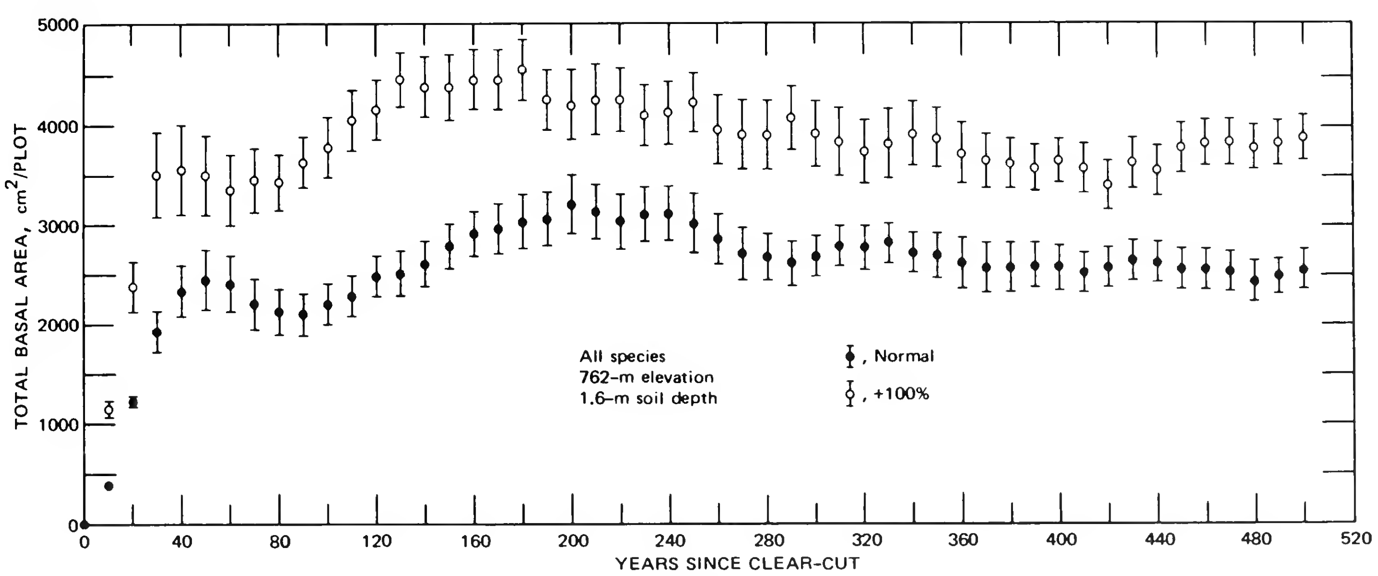
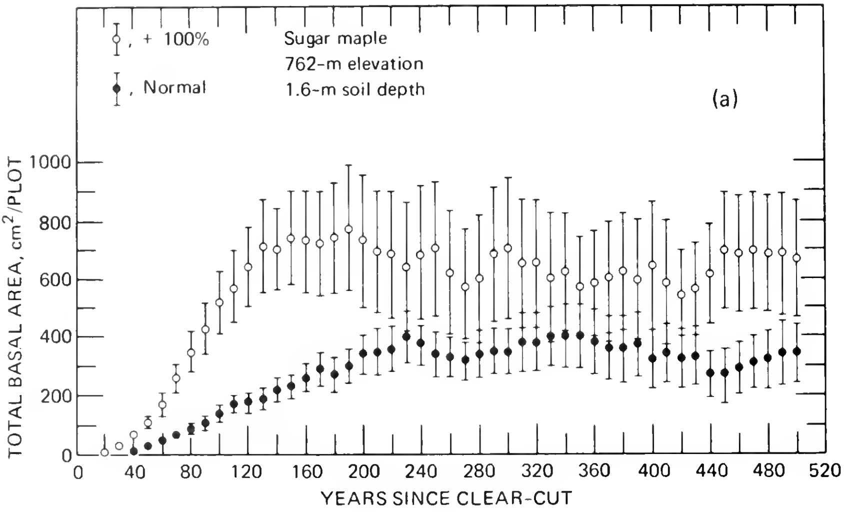


Fig. 4 Long-term trends in total basal area for simulated forest stands having trees with normal and 100% greater than normal annual growth increment. Because the simulations are stochastic and the random number sequence is different in the 100- and 500-year simulations, "normal" conditions in this figure are not necessarily identical to those of Fig. 2. Shown are 95% confidence intervals and means for 100 replicates.



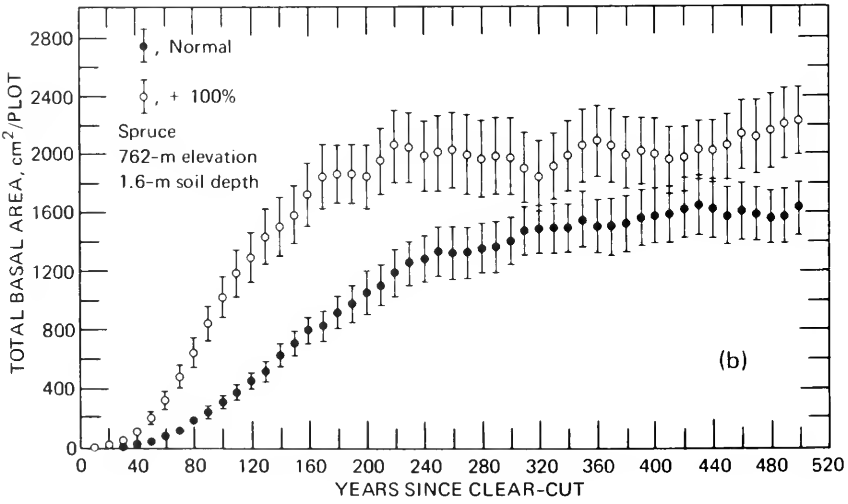
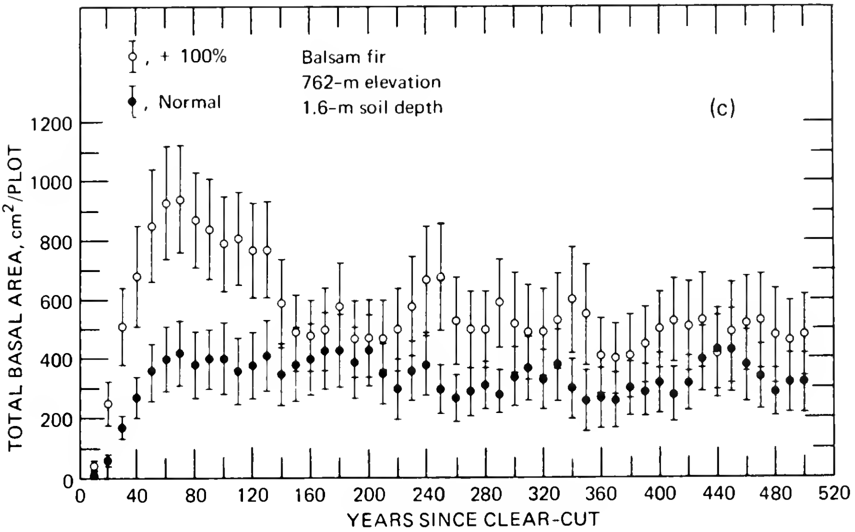


Fig. 5 Long-term trends in basal area contributed by sugar maple (a), spruce (b), balsam fir (c), and white birch (d). Conditions as in Fig. 4.


, + 100%
, Normal
Balsam fir
762-m elevation
1.6-m soil depth
(c)
TOTAL BASAL AREA, cm²/PLOT
0
200
400
600
800
1000
1200
0
40
80
120
160
200
240
280
320
360
400
440
480
520
YEARS SINCE CLEAR-CUT

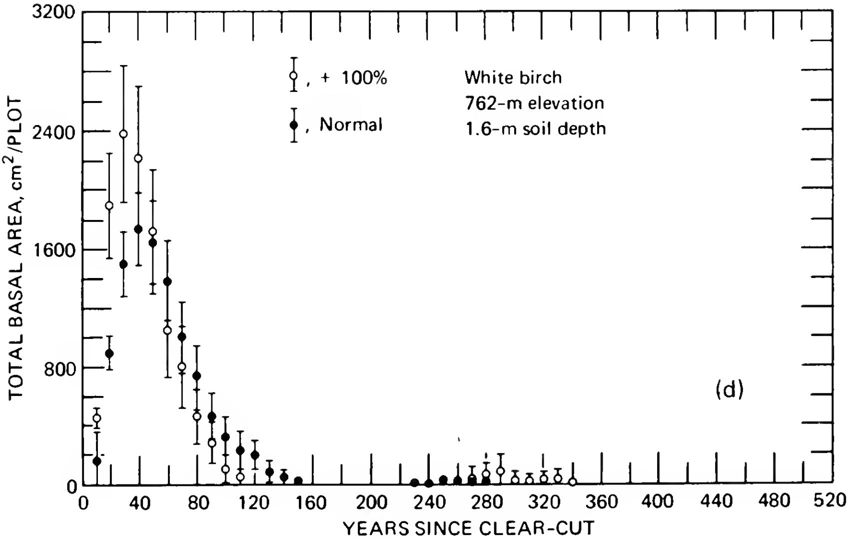

, + 100%
, Normal
White birch
762-m elevation
1.6-m soil depth
(d)
TOTAL BASAL AREA, cm²/PLOT
0
800
1600
2400
3200
0
40
80
120
160
200
240
280
320
360
400
440
480
520
YEARS SINCE CLEAR-CUT

TABLE 1 BASIC PARAMETERS

G = growth constant, C = leaf area constant, AGEMX = maximum age (years); D_{max} = maximum known diameter (cm), H_{max} = maximum known height (cm), b_2 and b_3 are constants in the equation $H = 137 + b_2 D - b_3 D^2$ relating height to diameter; DMIN and DMAX are minimum and maximum degree-days; WMIN and WMAX are minimum values for the index of evapotranspiration. [D. B. Botkin, J. F. Janak, and J. R. Wallis, Rationale, Limitations, and Assumptions of a Northeastern Forest Growth Simulator, *IBM Journal of Research and Development*, 16(2): 101–116 (1972).]

	G[a]	C[b]	AGEMX	Type[c]	D_{max}/H_{max}	b_2	b_3	DMIN[d]	DMAX[d]	WMIN	WMAX
Sugar maple	170	1.57[e]	200[f]	2	152.5[f]/4011[f]	50.9	0.167	2000	6300	300	
Beech	150	2.20[e]	300[f]	2	122[f]/3660[f]	57.8	0.237	2100	6000[g]	300	
Yellow birch	100	0.486[e]	300[f]	1	122[f]/3050[f]	47.8	0.196	2000	5300	250	
White ash	130	1.75	100	2	50/2160[f]	80.2	0.802	2100	10700	320	
Mountain maple	150	1.13[e]	25	2	13.5/500	53.8	2.00	2000	6300	320	
Striped maple	150	1.75	30	2	22.5/1000	76.6	1.70	2000	6300	320	
Pin cherry	200	2.45[h]	30	1	28[h]/1126[h]	70.6	1.26	1100	8000	190	
Chokecherry	150	2.45	20	1	10/500	72.6	3.63	600[f]	10000	155	
Balsam fir	200	2.5	80[f]	2	50/1830[f]	67.9	0.679	1100	3700	190	
Spruce	50	2.5	350[f]	2	50/1830[f]	67.9	0.679	600	3700	190	
White birch	140	0.486	80	1	46/1830[f]	73.6	0.800	1100	3700	190	600[i]
Mountain ash	150	1.75	30	2	10/500	72.6	3.63	2000	4000	300	
Red maple	240	1.75	150[f]	2	152.5[f]/3660[f]	46.3	0.152	2000	12400	300	

Values not otherwise referenced were developed during the course of the study.

[a] Growth constants adjusted for reasonable growth of individual tree in full sun with climate and soil factors equal to 1 (values of G will give ~⅔ of maximum diameter at ½ of maximum age starting from 0.5-cm stem).

[b] Actual leaf area in square meters is $\sim Cd^2/15$ for D in cm. [c] Type 1 is shade-intolerant; type 2 is shade-tolerant.

[d] Climatological ranges in growing degree-days, obtained by matching northern and southern limits of range maps in Fowells (1965) to January and July mean world isotherms. [e] Whittaker (1972). [f] Harlow and Harrar (1941).

[g] Northern strain. [h] Marks (1971). [i] Calculated for New York City.

birch no better than normal, and balsam fir reaches a high peak in the treated forest from which it declines. It is of interest that, as the forest approaches a steady state, the roles of the individual species in the treated and untreated forests become more difficult to distinguish, and eventually the importance of balsam fir is indistinguishable.

DISCUSSION

In the simulated forest the stochastic properties of birth and death tend to mask the effects of fertilization on the structure and productivity of the forest, while interactions among species buffer the ecosystem. If a real forest were less noisy, the effects of the treatment would be more readily distinguishable, but our normal forest is at least as noisy as the observed Hubbard Brook plots.

As can be seen in Fig. 4, by year 200 both treated and untreated forests reach a total basal area statistically equivalent to their respective year 500 values. Once this stable value is reached, there is no net change in the stored carbon, and the treated forest would cease to cause any further net change in the atmospheric CO_2 concentration. It is important to recognize that in our experiments the only change made was to increase annual diameter growth of each tree by a constant percentage; in particular, maximum allowable tree diameters, heights, and ages, as well as chance of death and sapling entry, have not been changed. It is possible that fertilization might change what we have considered to be the fundamental species constants given in Table 1, and it is even conceivable that, if the appropriate constants were properly scaled, the sole effect of CO_2 fertilization might be to compress the time scale and in no way change the final state of the forest.

A carefully managed monoculture, where unhealthy individuals were eliminated early in life and healthy individuals protected, could have quite different properties than a natural ecosystem of many species such as that modeled here. A monoculture might be managed so that the population growth resembled that of the simulated spruce during the first century following clear-cutting. Our simulation points out the importance of species interactions and suggests that the behavior of a natural mixed-species ecosystem is different in kind from the behavior of single species in monoculture.

In our discussion we have used basal area exclusively as an index of the forest's status. However, we made similar calculations for stem density, leaf weight, and total biomass. In general, stem density tends to decrease with increases in basal area; leaf weight and total biomass tend to increase in approximately the same proportion as basal area.

CONCLUSIONS

The simulated experiments suggest the following answers to the questions posed at the beginning of this paper. Unless the effect of CO_2 increase in the atmosphere is sufficient to fertilize the annual growth of each tree approximately 50% above normal, changes in the structure or productivity of the forest as measured by basal area would probably not be observable. Changes in net forest productivity would occur at this or higher levels for early stages in succession. The major long-term effects of such extreme fertilization would be on the standing crop, and this change is much less than that which a linear extrapolation would suggest. A 100% increase in the annual growth rate of every tree for every year produces a standing crop increase of approximately 40%.

The important and unexpected effect of such fertilization is to weight the environment in favor of shade-tolerant, long-lived species and against shade-intolerant, short-lived ones. As a result, the process of succession is hastened. However, the final relative importance of each species is changed only to a small degree.

We find these results reasonable yet intriguing. They point out the need for better data regarding the fundamental population characteristics of major tree species. Probably of most significance, the simulator suggests ways in which a community of interacting species has characteristics different in kind from carefully controlled and manipulated monocultures.

ACKNOWLEDGMENTS

This work was partially supported by grants from the Office of Water Resources Research and the National Science Foundation. This is contribution No. 37 of the Hubbard Brook Ecosystem Study.

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DISCUSSION BY ATTENDEES

Richardson: I thought this was an extremely interesting paper, but your model bypasses the difficult question of how great an increase of atmospheric CO_2 would be necessary to increase tree growth rates by 10, 20, 50, or 100%. Is there any rough estimate of this that you could give us, on the basis of presently available data?

Botkin: No, there are no data to indicate how much CO_2 produces how much growth increase for a community. I bypassed that by saying, "Suppose CO_2 did produce a growth increment, what would happen then? Suppose it produced a 50% increase, then what?" There are studies, however, that show *kinds* of growth. For example, there is a study that shows that quite a large increase in CO_2 doubled the litter production of birch seedlings.

Allen: Botkin's model predicts mixed stand response, assuming equal effects of CO_2 fertilization on all species. However, two points need to be investigated closely to determine first-order plant response. One need is to model realistically the physics of the CO_2 diffusion pathway from the atmosphere to the CO_2 fixation sites in leaves. The second need is to determine stomatal opening response to CO_2 concentration. I will describe briefly the predictions of a microclimate and CO_2 uptake model (SPAM) developed by Stewart at Dr. Lemon's project at Ithaca. The most important inputs to this model are photosynthesis-response functions of leaves to light and to CO_2 concentration, which are coupled to responses of stomatal diffusion resistance to light and to CO_2 concentration. Many other climatic and plant parameters of somewhat lesser importance go into this monoculture model.

The CO_2 uptake has been simulated over a daylight period for corn on the basis of plant and microclimatic data of Aug. 18, 1968, at Ithaca, N. Y. The simulations were run at 315 ppM and at 400 ppM, a 27% increase. If no stomatal closure occurred (typical of some terrestrial plants), the model predicted a 21% increase in daily total CO_2 uptake. If partial stomatal closure occurred, on the basis of corn data, the model predicted only a 9% increase in CO_2 uptake rates.

Plans are underway to extend this model to a complex ecosystem and even to the global scale. For an ecosystem, knowledge of the vertical and horizontal distribution of types of leaf material and their light responses and stomatal responses to ambient CO_2 concentration are required to predict increased CO_2 uptake due to increased background CO_2 concentration.

The SPAM model uses physics and physiology to predict first-order CO_2 uptake. The next questions to be answered are what the consequences are of the increased CO_2 uptake for local and global ecosystems and how fast the additional fixed carbon will be recycled. Botkin's model can give answers to these types of questions, but it does not handle adequately the physics and physiology of the initial CO_2 uptake.

Wright: Preliminary data on response of dominants in the Brookhaven oak–pine forest to CO_2 enhancement give strong indication that response of photosynthesis to CO_2 is anywhere from 50 to 100% as great as increase in percentage ambient CO_2. Such response was measured in September, May, and June for shoots in the canopy, below the canopy, and on seedlings on days ranging from full light to 25% full light. Response to CO_2 enhancement in increments, up to a maximum concentration of over 500 ppM, appears linear to 400 ppM and curvilinear to 500 ppM. Relative responses of different species varied considerably, with oaks advantaged more than pine.

CARBON FLOW AND STORAGE IN A FOREST ECOSYSTEM

DAVID E. REICHLE, BLAINE E. DINGER, NELSON T. EDWARDS, W. F. HARRIS,
and PHILLIP SOLLINS
Ecosystem Analysis Program, Environmental Sciences Division, Oak Ridge
National Laboratory, Oak Ridge, Tennessee

ABSTRACT

Results reported in this paper are the initial synthesis of data on ecosystem dynamics of carbon in a temperate deciduous forest. A model of the annual budget is developed for a mesic *Liriodendron tulipifera* forest which quantifies pools of carbon in ecosystem components and annual fluxes of carbon within the system. Gross primary production and net primary production by the forest were 1626 and 685 g C m^{-2} $year^{-1}$, respectively. Total ecosystem respiration of 1465 g C/m^2 was divided between autotrophic (941) and heterotrophic (524) sources. Total biomass was 8.32×10^3 g C/m^2, with an aboveground to belowground ratio of 4.2. Detrital mass (dead organic matter) in the forest ecosystem of 12,850 g C/m^2 substantially exceeded biomass. The forest carbon model is used to evaluate the storage, turnover, and atmospheric exchange of carbon by a forested landscape.

The chemical energy of organic molecules is the foundation on which the life-support system of the biosphere is based. From the photosynthetic fixation of carbon dioxide to the bioenergetic bases of all physiological processes in plants and animals, carbon is the common denominator of living systems. Biological systems, from organisms to regional ecosystems, are coupled by carbon circulation through a common atmospheric pool. But even now the importance of different ecosystems in influencing the rates and balances of these cycles is not definitely known. Although data are becoming available which suggest that terrestrial ecosystems, especially forests, have been underestimated in previous assessments of global carbon cycles (see Whittaker and Likens, 1972), it has been difficult to assess recent trends of carbon exchange and to extrapolate more than a few years into the future (Olson, 1970).

The biosphere may be studied at various levels of resolution, but analysis of the basic biological processes affecting the carbon cycle is dependent on an understanding of the driving forces of ecosystem components of the landscape, their internal dynamics, and the ecological mechanisms through which they are regulated (Reichle and Auerbach, 1972). Total-ecosystem analyses are based on the concept that the landscape is organized into logical patterns of self-sustaining, internally regulated, and dynamic components and that ecosystem metabolism not only is fundamental to the integrity and stability of the system itself but also is a viable approach to examining the carbon dynamics of large segments of the biosphere.

Although patterns are beginning to unfold for many ecological phenomena, relatively little is known about the dynamics, regulation, and stability of carbon cycles in natural ecosystems or about the quantitative differences and similarities in function between various types of ecosystems. In the following analysis of a temperate deciduous forest, a budget model of carbon pools in ecosystem components and annual fluxes within the system has been developed to evaluate the storage, turnover, and atmospheric exchange of carbon by a forested landscape.

SITE DESCRIPTION

The study site is a second-growth, mesophytic, deciduous forest located on karst topography within the U. S. Atomic Energy Commission reservation at Oak Ridge, Tenn. (35°55′N, 84°17′W). The forest is dominated by tulip poplar interspersed with various oaks (*Quercus velutina, Q. alba, Q. coccinea, Q. rubra,* and *Q. prinus*), short-leaf pine (*Pinus echinata*), and hickory (mainly *Carya tomentosa*). Understory species include redbud (*Cercis canadensis*), flowering dogwood (*Cornus florida*), and occasional black gum (*Nyssa sylvatica*), sourwood (*Oxydendrum arboreum*), red maple (*Acer rubrum*), and ash (*Fraxinus pennsylvanica*). Virginia creeper (*Parthenocissus quinquefolia*), woody hydrangea (*Hydrangea arborescens*), and Christmas fern (*Polystichum acrostichoides*) account for approximately 90% of the herbaceous biomass, although many other species are present.

The forest is established on a deep alluvial Emory silt loam soil. Height of the tallest tree is 30 m [42 cm diameter at breast height (DBH)], and the age of overstory is approximately 48 years. In 1962 the basal area of all trees $\geq$2.54 cm DBH was 19.2 m^2/ha (hectare) and in 1970, 22.1 m^2/ha. The leaf-area index is 7.12. Mean annual temperature is 13.3°C, mean annual precipitation averages 126.5 cm, and total solar radiation averages 123.5 kcal cm^{-2} $year^{-1}$.

CARBON DISTRIBUTION AMONG ECOSYSTEM COMPONENTS

Autotroph Aboveground Standing Crop

Analysis of the autotroph component of the forest includes components of the overstory and understory trees and the herbaceous stratum. Estimates of

TABLE 1

SUMMARY OF CARBON CONTENT AND PERCENT BIOMASS CONTRIBUTION OF WOODY SPECIES TO THE PRIMARY PRODUCER COMPONENT OF THE *LIRIODENDRON* FOREST AREA

Species (number of replicates is given in parentheses)	Carbon content ($\overline{X}$% + 1 SE)	Total aboveground biomass, %	
		Overstory	Understory
Liriodendron tulipifera (2)	49.9 ± 2.3	78.30	0.0
Cercis canadensis	ND*	3.28	1.71
Nyssa sylvatica (1)	47.9†	3.28	0.0
Oxydendrum arboreum (3)	52.2 ± 1.6	3.06	0.17
Pinus echinata (1)	45.8†	2.97	0.0
Sassafras albidum	ND	1.49	0.0
Juniperus virginiana	ND	1.06	0.0
Quercus spp. (7)	46.8 ± 1.6	1.04	0.35
Acer rubrum (4)	50.2 ± 0.7	0.78	0.33
Cornus florida (3)	52.0 ± 3.2	0.0	1.39
Fraxinus spp.	ND	0.0	0.65
Carya spp. (3)	51.6 ± 2.0	0.0	0.11
Mean carbon content (all species)	49.6		

*No data available.

†Value given is mean of duplicate determinations on pooled samples from a single tree.

autotroph aboveground biomass and rates of annual accumulation were based on allometric relations of weight of tree components and DBH (Sollins and Anderson, 1971; Harris, 1972) and periodic inventory of tree-diameter distribution (Sollins, 1972).

Conversion of woody organic matter to carbon was based on multiple carbon determinations using flame photometric detection procedures following high-temperature pyrolysis and catalytic hydrogenation (Horton, Shults, and Meyer, 1971). Where samples were available, seasonal variation in carbon content was determined. However, for most woody components the seasonal variation was not analyzed. Table 1 summarizes carbon content of major woody taxa and their relative abundance in the study area. Carbon values reported are either the mean of duplicate determinations of material from a single individual or the mean ±1 standard error (SE) where material from replicate individuals was available.

Liriodendron tulipifera comprises 78% of aboveground biomass. No other taxon contributes more than 5% of the total aboveground pool. Carbon content varied from 45.8 to 52.2%. However, variation within taxa was as great as variation among taxa. Therefore a carbon content of 49.6% was used in all calculations of standing crop of woody carbon and annual accumulation.

From the data in Table 2, the distribution of carbon in the aboveground portion of the autotroph component as of 1970 is estimated to be 8.32 kg/m^2. This estimate includes leaf carbon of 186 g/m^2 with the pool of 310 g/m^2, consisting of standing dead branch and bole material. The fraction of carbon in stump (1.02 kg/m^2) includes the central stump and large support roots within a radius of 0.6 m. Weight analysis of stumps suggests a stump-to-bole ratio of 0.20, which was used to estimate the weight of this component. Less than 10% of the total aboveground carbon was incorporated in the understory stratum and only 0.17% in the herbaceous (low shrub) stratum.

Autotroph Belowground Standing Crop

Underground organic-matter pools and associated physiological processes are the least accurately measured and least understood ecosystem component, but root processes are of at least equal importance to ecosystem function as the process of photosynthesis itself. Our analysis separates underground biomass into two components: stumps (discussed previously) and lateral roots beyond the stump radius. Soil cores and pits were used to estimate lateral-root biomass. Rooting-zone depth does not exceed 60 cm in the *Liriodendron* forest study area even though depth to bedrock is many meters. Therefore all unit-area root-carbon estimates are based on a depth of 60 cm.

Figure 1 summarizes the seasonal dynamics of the lateral root component. Averaging across sampling dates yields a mean annual lateral root standing pool of carbon of 650 g/m^2. Accumulation of carbon begins in the lateral root pool by July and continues into the late summer—early autumn. Considerable root dieback of organic material occurs in the fall—winter period. Explanation of the high value of lateral root organic matter in April 1971 awaits completion of confirmatory measurements in 1972 (Fig. 1). Annual fluctuation in climate of the preceding dormant season could be expected to influence pool size.

Olson (1968) reported a value (0 to 10 cm) of 890 g/m^2 organic matter (approximately 350 g C/m^2) for small and medium-sized roots (less than 10 cm diameter). Our analysis to a depth of 60 cm indicates that 30% of the lateral root organic matter is located in the upper 10 cm of soil. With this assumption, 1.17 kg C/m^2 was estimated from Olson's data for 1962 as a peak (early fall) standing crop of lateral root material, compared to 0.85 kg C/m^2 based on 1970 data.

Standing Crop of Detritus

Litter standing crop collected monthly at 25 randomly selected plots averaged 557 g/m^2, with the O_1 and O_2 litter accounting for 271 and 286 g, respectively (Table 3). Carbon content of O_1 litter was higher (46.5%) than that

TABLE 2

DISTRIBUTION OF CARBON (g/m^2) AND ANNUAL RATES OF CARBON INCORPORATION IN THE STANDING POOL OF WOODY MATERIAL (EXCLUSIVE OF LATERAL ROOT MATERIAL) AND FOLIAGE

(Unless otherwise indicated, 0.496 was used to convert organic matter to carbon)

Forest component	1970 standing pool of carbon, g/m^2					Annual net carbon accumulation, g/m^2 *			
	Bole	Branch	Stump†	Foliage‡	Total	Bole	Branch	Stump	Total
Liriodendron tulipifera	3820 (7694)§	1080 (2174)	763	122 (247)	5785	119	30	24	173
Other overstory trees	1230 (1746)	266 (537)	173	38 (76)	1707	−7	−3	−2	−12
Understory trees	290 (589)	105 (213)	87	26 (51)	508	3	1	1	5
Herbaceous cover¶					14				
Standing deadwood					310				
Total	5340	1451	1023	186	8324	115	28	23	166

*Carbon accumulation calculated from: (1) cumulative annual litterfall and (2) allometric estimation of weight from periodic DBH tally data.

†Stump standing crop (stump and support roots within an ~0.6-m radius) is estimated from stump : bole ratio of 0.20 with extrapolation to an area estimate from DBH tally data. Accumulation of carbon in stumps therefore is assumed to be directly proportional to bole increment.

‡Foliage carbon is calculated from tally data and allometric equations multiplied by carbon content of mature *Liriodendron* foliage (collected in September) exclusive of consumption.

§Values in parentheses are grams of organic matter.

¶Herbaceous biomass production is based on an average of estimates by Hoffman (unpublished manuscript), Taylor (unpublished data), Waller et al. (1965), and Cristofolini (1970). Carbon content (27.3%) is based on the average values for *Podophylum peltatum*, *Polystichum acrostichoides*, and *Hydrangea arborescens*.

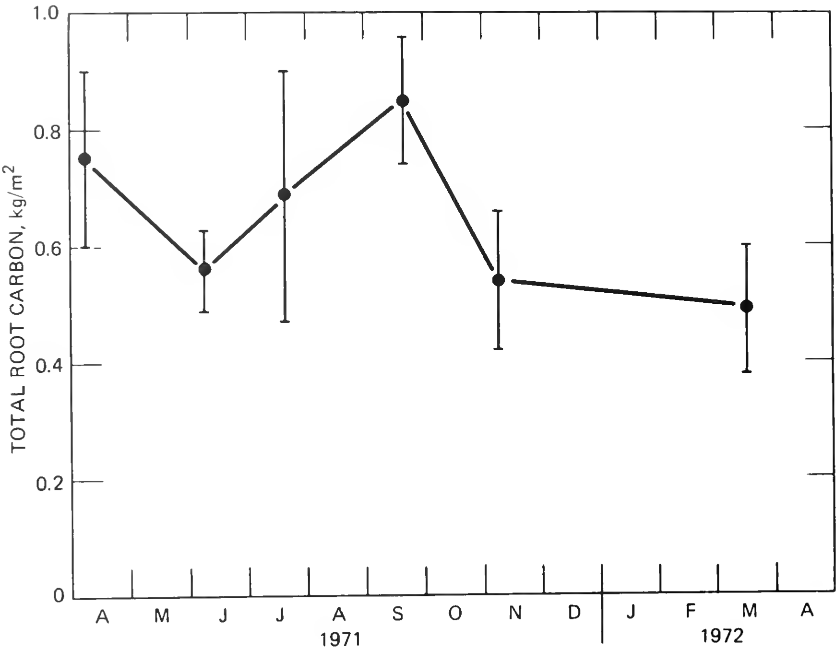

Fig. 1 Seasonal dynamics of lateral root carbon in the *Liriodendron* forest for the period April 1971 to March 1972. Net carbon accumulation (calculated by difference) equals 290 g/m^2, and root-carbon turnover (calculated by difference) amounted to 360 g/m^2 through March. A conversion factor of 0.387 was used to convert root organic matter to carbon. The smaller conversion factor reflects the greater ash content of underground material. Mean annual standing crop of lateral root carbon is 650 g C/m^2.

of O_2 (38.7%), giving a mean annual value for litter of 237 g C/m^2. No seasonal pattern of carbon concentration in litter was discernible. The total amount of O_1 litter carbon showed a decrease during the summer and an increase in the fall, whereas O_2 litter carbon increased gradually during summer and fall.

Soil organic matter decreased from 4.65% in the upper 10 cm to 1.25% at the 21- to 30-cm depth (Table 3). The total amount of carbon was calculated, assuming 58% carbon (Jackson, 1958), to be 12.3 kg C/m^2 to a depth of 75 cm.

Heterotrophic Carbon Pool

Calculations of canopy arthropod biomass were based upon weekly measurements of population densities per leaf and converted to unit area biomass using litterfall estimates of the number of leaves per square meter (Reichle and Crossley, 1967). Total biomass of herbivores averaged 243 mg (dry weight)/m^2 during the growing season, and predaceous arthropods averaged 61 mg/m^2 (Fig. 3). The numbers of leaf-feeding herbivores (geometrids; tree

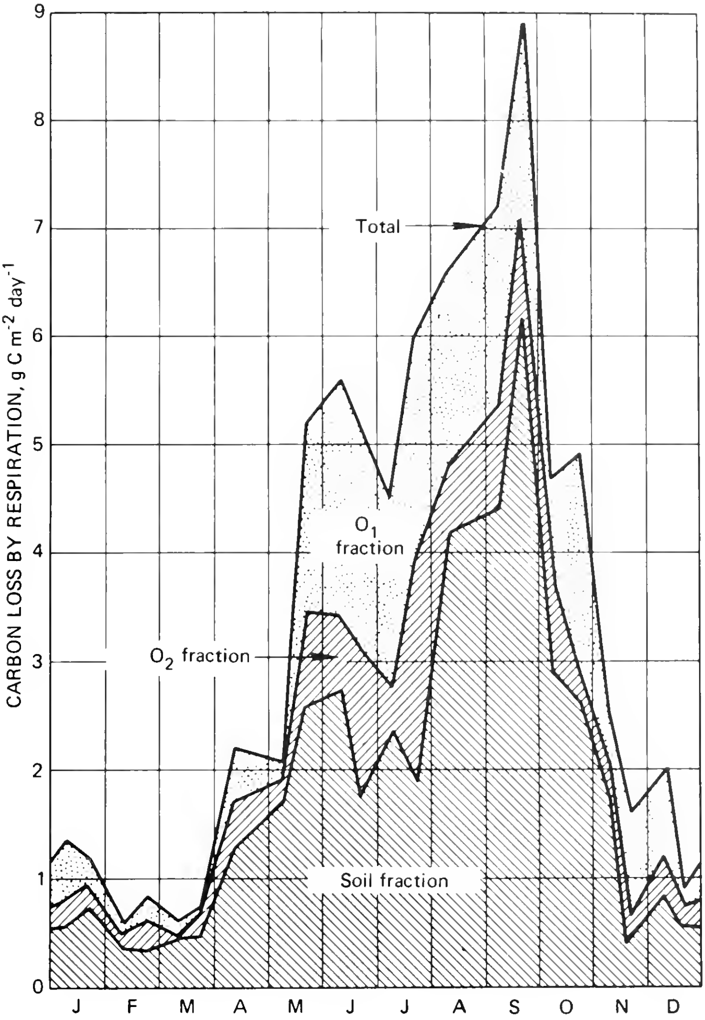

Fig. 2 **Seasonal pattern of forest-floor carbon evolution (in CO_2) measured in situ with an infrared-gas analyzer. Evolution was partitioned between O_1, O_2, and soil horizons using plexiglass sheets. All data points represent 24-hr means.**

crickets, *Oecanthus;* and weevils, *Odontopus calceatus*) progressively decreased during the growing season, but biomass ($\bar{x}$ = 170 mg/m^2) increased owing to the continued growth of individuals. The combined biomass (64 mg/m^2) of the cicadellid and aphid (*Macrosiphum liriodendroni*) sap feeders decreased by early summer owing to heavy predation by aphidlions (*Chrysopa*). Psocoptera (8 mg/m^2) and four species of omnivorous ants (2 mg/m^2) complete the nonpredaceous component of canopy-insect biomass. Predators (almost exclu-

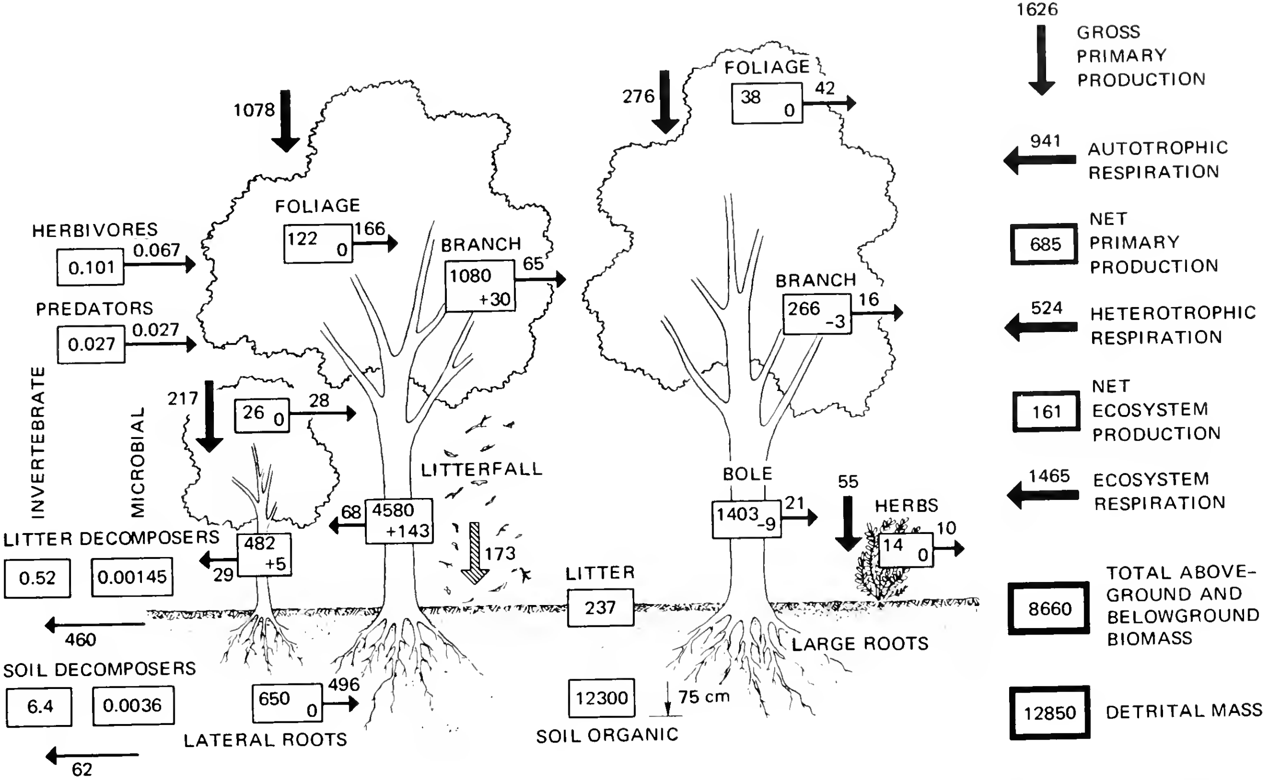

Fig. 3 Pictorial presentation of the carbon cycle in a mesic hardwood-forest ecosystem at Oak Ridge National Laboratory. Structural components of the ecosystem have been abstracted as compartments, with the major fluxes through the system illustrated by arrows. From left to right, trees represent understory, dominant tulip poplar, and other overstory trees. Values in upper left of compartments are annual standing crops, and those in the lower right are annual increment. Annual fluxes are shown on appropriate arrows: lateral arrows indicate respiratory losses and vertical arrows represent photosynthetic fixation. Units of measure are grams of carbon per square meter and grams of carbon per square meter per year for compartment increments and fluxes. Summaries of ecosystem metabolism and standing crop are shown at the right.

sively spiders) averaged 61 mg/m^2. Using 45% as the mean analyzed carbon content of insect tissue gives values for the carbon pools in herbivores and predators of 101 and 27 mg C/m^2, respectively.

The majority of litter macroinvertebrates (77% by number and 88% by weight) belong to 10 taxonomic groups: Araneae, Chilopoda, Coleoptera, Collembola, Diplopoda, Diptera, Hymenoptera, Lepidoptera (larvae), Orthoptera, and Pulmonata. Densities ranged from a low of 690 individuals per square meter in April to a high of 2700 individuals per square meter in July. Mean annual biomass was 842 mg (dry weight)/m^2 (Moulder and Reichle, 1972). Microinvertebrates in litter averaged 5.9×10^4 individuals per square meter with a biomass of 342 mg/m^2; soil microinvertebrates numbered 3.9×10^4 individuals per square meter and had a biomass of 220 mg/m^2 (McBrayer and Reichle, 1971). Earthworms (14 g/m^2), primarily *Octolasium*, constituted the bulk of the soil invertebrate biomass. Total aboveground biomass was 1.2 g/m^2; belowground invertebrate biomass averaged 14.2 g/m^2. With an average carbon content of 45%, the belowground carbon pool is 6.4 g C/m^2. The aboveground carbon pool was calculated by using a 20% carbon value for heavily skeletonized chilopods and snails that comprise about 20% (0.44 g/m^2) of the biomass and a 45% carbon content for the remainder of the fauna. The aboveground invertebrate carbon pool is 0.52 g C/m^2.

Microbial populations, determined from biweekly plate counts, varied throughout the year with changes in temperature and moisture. Moisture is the dominant limiting factor at temperatures > 10°C. Carbon content of total microflora in litter was 1.45 mg C/m^2, apportioned approximately 60% to fungi and 40% to bacteria. The carbon pool in total soil microflora was 3.56 mg C/m^2, with approximately 65% in fungi and 35% in bacteria (Ausmus, personal communication). Densities per gram substrate for bacteria were 2.3×10^8 for O_1 litter, 2.5×10^8 for O_2 litter, and 5.6×10^6 for A_1 soil to 5 cm; fungal densities were 2.7×10^6 for O_1 litter, 124×10^6 for O_2 litter, and 0.3×10^6 for A_1 soil to 5 cm (Edwards, 1972).

Annual Carbon Increment and Changes in Pool Sizes

Table 2 summarizes rates of annual accumulation in aboveground autotroph components based on standing-crop differences between 1962 and 1970 (Sollins, 1972). Saplings unaccounted for in 1962, but present in 1970, were assumed to have been added at a uniform annual rate over the 8-year period. Tree mortality also was assumed to have occurred at a uniform rate. Net contribution to a standing dead carbon pool of bole and branch material was calculated to be 50 g C m^{-2} year^{-1}. A net total of 166 g C m^{-2} year^{-1} accumulated in woody structural components. Over the 8-year period, other overstory components decreased, whereas understory trees showed a slight gain (Table 2). Stump increment was assumed to be directly proportional to bole increment.

Lateral root production was estimated from the difference between maximum and minimum standing crop (Fig. 1). Between June and September, net lateral root carbon increased by 290 g C/m^2. Lateral root carbon increase was approximately 80% of the amount fixed in aboveground and stump material (Table 2). Root-carbon decrease is likely an underestimate of root death because of mortality and disappearance between sampling periods. For example, Cox (1971) reported that 20% of roots $\leqslant$0.5 cm in diameter are dead at any time during the growing season.

Net change in carbon-pool size for the root compartment (again based on differences in standing crop) between September and March (Fig. 1) indicates root dieback of 360 g C/m^2. Apparent root mortality during the dormant season contributes carbon to the decomposer substrate and eventually to the soil carbon pool, but loss of carbon is probably confounded with the vernal flux of labile carbohydrates to the aboveground components. Subsequent calculations assume that accumulation of lateral root carbon equals annual turnover to the decomposer substrate.

Foliage biomass was estimated from the allometric relation of total leaf weight to DBH (Sollins, 1972). However, cumulative annual litterfall estimates were 40% less than foliage weight determined allometrically. Comparison of unit leaf weights of mature leaves (0.37 to 0.39 g per leaf, Dinger, unpublished data; Reichle and Crossley, 1967) to unit leaf weight of abscissed foliage (Olson, 1971) suggests a net translocation of approximately 30% of mature foliage weight prior to abscission—56 g C m^{-2} year^{-1}. Other sources of carbon loss not accounted for are leaching of organics during the season and in the litter traps.

CARBON FLUXES IN THE ECOSYSTEM

Foliar Carbon Dioxide Exchange

Net photosynthesis and respiration of yellow poplar (*Liriodendron tulipifera*) leaves were determined under natural temperature and light conditions by means of a gaseous-exchange apparatus incorporating an infrared analyzer and inflatable polyfilm chambers (Dinger, 1971). Data from 450 chamber hours of observations gave a mean "daylight" (i.e., light intensity $\geqslant$0.015 cal cm^{-2} min^{-1}) CO_2 intake rate of 6.4 mg g^{-1} (dry weight foliage) hr^{-1} (Table 4). "Dark" ($<$0.015 cal cm^{-2} min^{-1}) respiration losses were 0.6 mg/hr. On the basis of 12 hr of "daylight" and an equal "dark" period, mean daytime CO_2 uptake rates would be 77 mg/g foliage and dark respiration losses 7.0 mg/g, resulting in a net diurnal CO_2 absorption of 70 mg/g. If we assume these net absorption rates to be representative for the entire season (180 days), annual net daily CO_2 fixation per unit dry weight foliage is 12.6 g/g, and dark respiration removes 1.2 g/g, or 9.8% of total daily CO_2 uptake.

Net carbon dioxide uptake for other canopy trees was calculated from the literature (Table 4). Net daytime CO_2 uptake by yellow poplar (12.6 g/g) was

TABLE 3

CARBON FLUX TO THE FOREST FLOOR BY LITTERFALL AND CARBON STANDING CROP*

		Litter		
	Type	**Weight, g/m^2**	**Carbon, % (annual mean + SE)**	**Carbon, g/m^2**
Litterfall	Leaves			
	Tulip poplar	218	49.5 ± 0.6	108
	Miscellaneous	107	45.7 ± 0.9	49
	Twigs	17	47.0 ± 1.0	8
	Reproductive parts	16	48.3 ± 0.8	8
	Total	358		173
Litter standing crop	O_1 horizon	271	46.5 ± 0.3	126
	O_2 horizon	286	38.7 ± 0.6	111
	Total	557		237

		Soil		
Soil depth, cm	**Bulk density, g/cm^3**	**Organic matter,† %**	**Carbon,‡ %**	**Carbon, g/m^2**
0 to 10	0.99	4.65	58.0	2,670
11 to 20	1.27	2.14		1,580
21 to 30	1.52	1.25		1,100
31 to 50	1.19	1.74	58.0	2,400
51 to 75	1.12	2.77		4,500
Total				12,250

*Litterfall collected over a 3-year period in 20 plastic tubs (0.15 m^2) placed at random within a 500 m^2 plot. Mean litter standing crop determined from monthly samples through 1 year. Carbon values were determined on randomly selected litterfall and litter standing-crop samples.

†By Walkley–Black procedure as described by Jackson (1958).

‡The conventional 58% carbon value is generally accepted by soil biologist as the average percent carbon in soil organic matter (Jackson, 1958).

multiplied by the ratio of the mean maximum net photosynthetic rate reported for these species to the mean maximum rate obtained for yellow poplar of 6.5 mg dm^{-2} hr^{-1} or 8.1 g g^{-1} hr^{-1}. This product was considered to be the annual net daytime CO_2 uptake for the species in question, corrected for variations due to fluctuations in environmental factors similar to those impinging on yellow poplar in the ecosystem being studied. Total dark respiration for these was estimated in a similar fashion, using annual dark CO_2 losses for yellow poplar and the appropriate gaseous exchange ratio (Table 4). The mean of net daytime

TABLE 4

CARBON DIOXIDE EXCHANGE RATES FOR TREE SPECIES OCCURRING IN THE TULIP POPLAR FOREST

Species	Mean net photosynthesis		CO_2 exchange ratio (Other species: *Liriodendron*)	Annual CO_2 flux	
	mg CO_2 dm^{-2} hr^{-1}	mg CO_2 g^{-1} hr^{-1}		Net daytime uptake, g/g	Dark respiration, g/g
Liriodendron tulipifera	6.5	8.1		12.55	1.23
Quercus alba†	5.2		0.80	10.04	0.98
Quercus borealis maxima†	5.5		0.85	10.67	1.05
Quercus macrocarpa‡	6.5		1.00	12.55	1.23
Acer saccharum‡	4.6		0.71	8.91	0.87

*Net daytime CO_2 uptake for all species was calculated from ratios of maximum net photosynthetic rate measured for *Liriodendron* in situ to maximum net photosynthetic rate reported in the literature for other species.

†Kramer and Decker (1944).

‡Wuenscher and Kozlowski (1970).

TABLE 5

NET CARBON DIOXIDE UPTAKE AND DARK RESPIRATION FOR MAJOR VEGETATIONAL COMPONENTS IN THE TULIP POPLAR FOREST

Vegetation component	Leaves/area,* g/m^2	Annual daytime CO_2 uptake		Annual dark respiration	
		Per leaf g/g	Per area, g/m^2	Per leaf, g/g	Per area, g/m^2
Yellow poplar	247	12.6	3100	1.23	303.8
Associated overstory	76	10.5	801	1.03	78.3
Understory	51		533		52.0
Total			4434		434.1

*All values on dry weight basis.

CO_2 uptake (10.5 g/g) and dark respiration (1.0 g/g) rates estimated for associated overstory species was used to calculate total carbon dioxide flux for this component.

Net CO_2 uptake per 24-hr period over the entire growing season is calculated to be 11.3 g/g of foliage, using 70 mg/g net CO_2 intake for *L. tulipifera* and subtracting respirational losses. This estimate compares to values of 14.5 g/g and 8.9 g/g for white oak and scarlet oak, respectively, in the Brookhaven forest (Botkin, Woodwell, and Tempel, 1970). Multiplication of CO_2 uptake per gram of leaf by leaf biomass (Table 2) yielded a daytime CO_2 uptake for yellow poplar equivalent to 3100 g/m^2 (Table 5). Uptake by associated overstory species became 801 g/m^2. Dark respiration by these components resulted in loss of 382 g/m^2. Carbon dioxide uptake and release by understory species were considered as being proportional to the leaf biomass of this component, yielding an annual CO_2 uptake and dark respiration of 533 g/m^2 and 52 g/m^2 respectively.

When contributions of all vegetation components were added up, total daytime CO_2 uptake for the forest was 4.43 kg m^{-2} $year^{-1}$ and dark respiration was 0.43 kg m^{-2} $year^{-1}$, resulting in an annual net CO_2 uptake equivalent to 4.00 kg m^{-2} $year^{-1}$. Converting CO_2 fluxes to carbon resulted in net carbon uptake of 1.09 kg C m^{-2} $year^{-1}$. Dark respiration resulted in the release of 0.12 kg C m^{-2} $year^{-1}$. A lower bound on gross carbon fixation was approximated by assuming that daytime respiration was equivalent to nighttime rates and adding leaf respiration to daytime CO_2 uptake. The procedure neglected photorespiration, a phenomenon that has yet to be evaluated in most forest species. Thus the first estimate of total annual carbon influx (net annual uptake plus two times dark respiration) by woody vegetation is 1.33 kg C m^{-2} $year^{-1}$ based on initial gas-exchange data.

Respiration of Woody Tissues

Carbon efflux due to respiration of lateral roots was estimated from manometric determinations of various-sized yellow poplar roots. Respiration rates (CO_2 efflux) at 15°C were 0.13 mg g^{-1} (dry weight) hr^{-1} for roots <0.5 cm in diameter, and 0.08 mg g^{-1} hr^{-1} for larger roots. Multiplying these CO_2 respiration rates by the total standing crop of two lateral root-size classes yielded an hourly CO_2 release of 0.07 g m^{-2} hr^{-1} ($\leqslant 0.5$-cm diameter roots) and 0.14 g m^{-2} hr^{-1} (>0.5-cm diameter roots). On an annual basis, respiration by small roots would result in release of 0.59 kg CO_2 m^{-2} $year^{-1}$. Larger roots would respire 1.23 kg CO_2 m^{-2} $year^{-1}$ resulting in 1.82 g CO_2 m^{-2} $year^{-1}$ total efflux. Conversion of these values to carbon flux yields a total annual carbon loss by the root component of this system equal to 0.496 kg C m^{-2} $year^{-1}$.

Shoot respiration data for *Fagus sylvatica* (Möller et al., 1954) were used for estimation of carbon efflux by this component of the system. Branch tissue was assumed to respire 0.11 g CO_2 g^{-1} $year^{-1}$ and bole tissues 0.03 g g^{-1} $year^{-1}$. With these provisional values and standing crop of bole and branch weight (Table 2), total respiration by these components was estimated to be equal to 593 g CO_2 m^{-2} $year^{-1}$ (branch = 322 g/m^2, bole = 271 g/m^2) or a carbon equivalent of 162 g C m^{-2} $year^{-1}$ total annual carbon loss due to stem respiration, excluding stumps.

Annual net daytime carbon influx by vegetation was estimated at 1.21 kg C m^{-2} $year^{-1}$. Leaf respiration resulted in a loss of 0.12 kg C m^{-2} $year^{-1}$, yielding a net carbon uptake equal to 1.02 kg C m^{-2} $year^{-1}$. Respiration by shoot and root tissues consumed 0.66 kg C m^{-2} $year^{-1}$ of fixed carbon, resulting in a gas-exchange estimate of net carbon accumulation of 0.43 kg C m^{-2} $year^{-1}$ by woody vegetation.

Heterotrophic Respiration

Carbon dioxide evolution rates from the forest floor were measured for 24-hr intervals biweekly with an infrared gas analyzer, using a technique that permitted partitioning CO_2 flux between O_1 litter, O_2 litter, and soil (Edwards, Van Hook, and Rau, 1971). Seasonal patterns of respiration corresponded primarily to fluctuations in temperature and moisture (Fig. 2). Carbon evolved as CO_2 from the forest floor was 1.04 kg/m^2, with 55.4% of this total derived from root and soil respiration, 29.5% from the O_1 litter, and 15.1% from the O_2 litter. Measured decomposer respiration was equivalent to 0.51 kg C m^{-2} year^{-1}, and root respiration accounted for 0.496 kg C m^{-2} year^{-1}. This is similar to forest-floor flux values of 0.71 to 0.79 kg C m^{-2} year^{-1} for an oak forest in Minnesota (Reiners, 1968) and considerably higher than the 0.41 kg C m^{-2} year^{-1} reported by Witkamp (1966) for a nearby oak forest in Tennessee.

In contrast to in situ measurements of respiration by heterotroph decomposers, respiration of foliage-feeding insects was estimated from body-size metabolism-regression equations (Reichle, 1971). Using mean body size for each age-class for the various insect species (Reichle and Crossley, 1967), respiration rates were calculated for herbivore and predator trophic levels. Total annual respiration by herbivores amounted to 0.067 g C m^{-2} year^{-1}, and that for predatory insects was 0.027 g C m^{-2} year^{-1}.

Litterfall and Tree Mortality

Annual litterfall averaged 358 g (dry weight) m^{-2} year^{-1} (Table 3). Tulip poplar leaves accounted for 61.3% of the total litter input, other leaves 28.9%, twigs 5.2%, and reproductive parts 4.6%. Carbon content of 3 of 20 samples for each collection period averaged 49.5% in tulip poplar leaves, 45.7% in miscellaneous leaves, 47.0% in twigs, and 48.3% in reproductive parts. Using these percentages an annual total carbon input to the forest floor by litterfall was calculated to be 173 g C/m^2. Seasonal patterns of carbon input to the forest floor by litterfall showed an expected large input in the fall and a lesser input in the spring. Spring litterfall consisted primarily of reproductive parts and twigs. Carbon concentrations in individual groups showed no significant seasonal patterns.

Insect Consumption

The loss of photosynthetic surface area in the canopy through insect grazing varied between years, as well as during the growing season. In 1965, leaf holes accounted for 5.6% of leaf area, although this was greater than the actual consumption (1.9%) due to hole expansion in growing leaves. In 1966, loss of foliage area was 10.1% (3.4% consumed); and in 1967 there was a foliage loss of 7.3% due to 2.5% leaf-area consumption (Reichle et al., in preparation). Within a span of only 3 years, insect consumption varied by a factor of nearly 2. Foliage production in the *Liriodendron* forest amounts to 186 g C/m^2. Using a 50% mean carbon content of leaves shows this flux to be 4.5 g C m^{-2} year^{-1}. Aphids return an estimated 0.5 g C m^{-2} year^{-1} in honeydew, most of which is washed off the surfaces of leaves by precipitation (Van Hook, personal communication).

TABLE 6

CARBON BUDGET FOR A *LIRIODENDRON* FOREST AT OAK RIDGE, TENN.*

	Destination compartment													
		Yellow poplar			Misc. overstory			Understory						
Source compartment	Atmosphere	Leaf	Branch	Bole & stump	Leaf	Branch	Bole & stump	Leaf	Branch, bole & stump	Herbaceous	Lateral roots†	Consumers	Standing dead	Litter	Soil carbon
Atmosphere		(1078)† 846			(276)† 219			(217)† 146		(55)					
Yellow poplar															
Leaves	166		(103)	(211)							(492) (260)	3		103	
Branch	65												0	8	
Bole & stump	68												0		
Misc. overstory															
Leaves	42					(23)	(31)				(153) (96)	1		26	
Branch	16												6	4	
Bole & stump	21												19		
Understory															
Leaves	28								(64)		(105) (34)	<1		19	
Branch, bole, & stump	29												26	4	
Herbaceous	10										(36)	<1		9	
Lateral roots	496													290	
Consumers	0.094													5	
Standing dead	2													(49)	
Litter	460														?
Soil carbon	62														

*All values are $g\ C\ m^{-2}\ year^{-1}$. Values in parentheses were derived by assuming conservation of mass for various compartments.

†Upper value derived by solving root conservation of mass equation, lower value by solving each leaf equation. Upper value was used in other calculations.

ECOSYSTEM ANALYSIS

Forest Carbon Budget

Although data may exist in great detail for parts of the ecosystem, synthesis is necessary before the behavior of the entire system can be described. The annual carbon budget for the ecosystem is one way of examining productivity and energy flow in the forest. In a budget the system is divided into storage compartments connected by transfer pathways. Data must include both the fluxes of carbon transferred along each pathway during the course of the year and the amount by which each compartment level changes during the same time period. Such budgets represent initial steps in the construction of dynamic simulation models.

Ecosystem carbon budgeting follows the principle of conservation of mass, namely, $\Delta Q = \Sigma I - \Sigma L$, where ΔQ is the change in compartment level, ΣI is the sum of all incomes to compartment Q, and ΣL is the sum of all losses. In the carbon budget for the *Liriodendron* forest (Fig. 3), some values were calculated by assuming conservation of mass and are appropriately indicated in Table 6. In several cases, information concerning transfers could be derived by two independent calculations. Thus translocation of carbon from leaves to lateral roots was estimated by solving the mass-balance equation for the lateral-root compartment and apportioning translocation among the leaf compartments in proportion to their biomasses. The same fluxes were also evaluated by solving each leaf-mass-balance equation for the carbon transfer out of leaves to lateral roots. Both estimates are shown in Table 6.

The Carbon Cycle

Although concise and mathematically balanced, the matrix representation of the forest carbon budget (Table 6) does not easily permit ecological interpretation; a pictorial form of the budget is presented in Fig. 3. Only photosynthetic fixation, respiratory losses, and compartment carbon levels and increments are shown. On the right-hand side, the metabolic parameters for the system have been summarized. Gross primary production (GPP) was estimated at 1.51 kg C m^{-2} $year^{-1}$, net primary production (NPP) was 0.685 kg C m^{-2} $year^{-1}$, and net annual increment (annual change in compartment levels) of autotrophs was 0.17 kg C m^{-2} $year^{-1}$. Autotrophic respiration (R_A) of 0.941 kg C m^{-2} $year^{-1}$ and heterotrophic respiration (R_H) of 0.524 kg C m^{-2} $year^{-1}$ sum for a total ecosystem respiration (R_E) of 1.330 kg C m^{-2} $year^{-1}$. Heterotrophic respiration was 31% of R_E and was almost entirely a consequence of decomposer activity. Compartment carbon value (standing crop) for autotrophs was 8.66 kg C/m_2 of which 19% (1.67 kg/m^2) consisted of roots. Heterotrophic biomass was estimated at 7.05 g C/m^2, and detritus (including standing deadwood and litter) amounted to 12.85 kg C/m^2.

Root respiration rates may have been overestimated because the largest size class used in respiration studies was ~3 cm in diameter, whereas many roots included in the biomass estimates were much larger. Total root respiration could have been overestimated due to decreasing respiration rate with increasing root diameter. The budget value for litter and soil respiration (exclusive of root respiration) was derived by summing all inputs of detritus and assuming no annual increment in detritus. When added to the root-respiration estimate, CO_2 evolution from the forest floor was estimated to be 1.02 kg C m^{-2} $year^{-1}$ compared to the measured value of 1.04 kg C m^{-2} $year^{-1}$. This agreement suggests that, in spite of the potential for revising estimated root respiration, present approximations are realistic. The two independent estimates of carbon translocation to roots differed by only 20% for all three groups of trees (yellow poplar, other overstory, and understory), which is not serious considering the preliminary nature of the data on which they are based. Annual root turnover is probably underestimated, and it is not presently possible to determine the error in estimates of branch and bole respiration of any species and of foliar gas exchange for species other than tulip poplar.

DISCUSSION

Fundamental to analysis of the carbon cycle in ecosystems is an understanding of the functional relationships between photosynthesis, respiration, and productivity of the system. Thus the annual increment of carbon in the ecosystem or NEP (net ecosystem production) after Woodwell and Botkin (1970) is

$$\mathrm{NEP} = \mathrm{GPP} - (R_A + R_H)$$

where $\mathrm{GPP} = \mathrm{NPP} + R_A$, and the equation may be rewritten in the form

$$\mathrm{NEP} = \mathrm{NPP} - R_H$$

Solution of these equations, with quantification of the contribution of various subsystem components to carbon pools and fluxes, is a primary objective of ecosystem analyses. Relationships between pools and fluxes, seasonality and variability of these parameters need to be explored by comparison of data from different ecosystems. In this manner the pattern of carbon dynamics in terrestrial landscapes will begin to unfold.

The most comprehensively analyzed ecosystem to contrast with our *Liriodendron* forest is the more xeric oak–pine forest at Brookhaven National Laboratory (Woodwell and Botkin, 1970). The mesic Oak Ridge forest has a total standing crop of 8.66 kg C/m^2 and a NPP of 685 g C m^{-2} $year^{-1}$. The respective values for the oak–pine forest can be calculated from biomass and estimated carbon content to be 5.96 kg C/m^2 and 598 g C m^{-2} $year^{-1}$. Relative productivity, the ratio of NPP to standing crop, is higher in the oak–pine forest

(10%) than in the tulip poplar forest (8%). The R_A by the oak–pine forest is lower at 675 g C m^{-2} $year^{-1}$ than the tulip poplar forest at 941 g C m^{-2} $year^{-1}$, and the respective ratios of R_A to standing crop are identical at 0.11. The GPP by the Oak Ridge forest was at least 1.63 kg C m^{-2} $year^{-1}$ compared to 1.36 kg C m^{-2} $year^{-1}$ for the Brookhaven forest, although the respective ratios of NPP to GPP were essentially identical at 0.42 and 0.45.

Estimates of NEP for the two forest ecosystems were substantially different. The NEP for the open oak–pine forest was between 271 and 294 g C m^{-2} $year^{-1}$ (depending on whether allometric or gas-exchange values were used to make the calculation), and NEP for the *Liriodendron* forest was 161 g C m^{-2} $year^{-1}$. Although the tulip poplar forest had higher GPP and NPP, its higher total R_E of 1.47 kg C m^{-2} $year^{-1}$ (compared to 1.01 kg C m^{-2} $year^{-1}$ for the oak–pine forest) resulted in a lower NEP. The higher relative respiration of the *Liriodendron* forest (R_E/NEP) of 9.1 compared to approximately 3.6 for the oak–pine forest reflects several fundamental differences between internal components of the two ecosystems.

The distribution of standing crop between aboveground and belowground components of the two forests varies severalfold. Whereas the oak–pine forest with a standing crop of 5.96 kg C/m^2 has an aboveground to belowground ratio of 1.8, the tulip poplar forest has a ratio near 4.2 for its biomass of 8.66 kg C m^{-2} $year^{-1}$. Generally, the respiration of belowground woody components, primarily fine roots, is higher than that of nonphotosynthetic aboveground biomass. The R_H in the mesic Oak Ridge forest (524 g C m^{-2} $year^{-1}$) was nearly twice that of the more xeric forest at Brookhaven. This discrepancy was not simply due to the magnitude of the R_E values but rather to a more basic apportionment of R_E between R_A and R_H; the ratio of R_A/R_H for the oak–pine forest was 2.5 but only 1.8 in the tulip poplar forest. In these parameters may lie one fundamental difference in NEP between the two forest ecosystems.

Although the tulip poplar forest annually loses 522 g C/m^2 through decay, the oak–pine forest turns over only 360 g C m^{-2} $year^{-1}$. For the mesic deciduous forest, decay amounts to an annual turnover of 4.1% of the detritus carbon pool of 12.85 kg C m^{-2} $year^{-1}$. Approximately 60% of the total carbon in the tulip poplar forest (21.51 kg C/m^2) is in the detritus pool. With an estimated NEP of 161 g C m^{-2} $year^{-1}$ and an annual woody increment of 168 g C m^{-2} $year^{-1}$, the carbon pool in litter and soil detritus remains in equilibrium according to our initial conditions. This would not be so for the oak–pine ecosystem, where a higher NEP to standing-crop ratio of 0.05 to 0.02 for the tulip poplar forest reflects continuing increase of carbon pools in both standing crop and soil organic matter. The sources and rates of carbon accumulation in soil are multiple. In the *Liriodendron* forest, annual decomposition respiratory losses account for 522 g C m^{-2} $year^{-1}$; 228 g C m^{-2} $year^{-1}$ from litterfall, dead bole and frass inputs is less than the additional 294 g C m^{-2} $year^{-1}$ root death required to keep the detritus carbon pool in equilibrium. Independent estimates of up to 360 g C m^{-2} $year^{-1}$ root death from harvest data indicate that the calculated input of root carbon to detritus is not unreasonable.

CONCLUSIONS

There are two major reservoirs for carbon in the biosphere exclusive of incipient fossil fuels: the oceans and the terrestrial landscapes of which forests comprise one-third the area and two-thirds of the total terrestrial carbon pool (Olson, 1970; Keeling, 1970). In varying degrees the assimilation of organic matter by ecosystem components of the biosphere compensates for some of the excess CO_2 (increasing at 0.2% or 0.7 ppM/year) released by the combustion of fossil fuels. In addition, the clearing of land continues to release much carbon from tree standing crop and humus pools, which suggests that this ecosystem impact has had a large historic effect on the world's carbon budget. Early International Biological Program synthesis of research (Olson, 1970) indicates that terrestrial plants absorb substantially more carbon by photosynthesis than do aquatic plants. Keeling (1970) has recently used Brookhaven estimates that the biosphere would respond to increased atmospheric CO_2 by an approximate 5 to 8% increase in primary production per 10% increase in atmospheric CO_2. All these factors underscore the importance in understanding the ecological factors affecting the carbon cycle in local and regional ecosystems.

Residence times of carbon in components of forest ecosystems vary considerably, depending on input and output fluxes as well as pool sizes. Some components such as foilage have a turnover time of 1 year or less, whereas others such as small roots may have a surprisingly rapid turnover rate (350 g C m^{-2} $year^{-1}$/1670 g C m^{-2} = 0.21 $years^{-1}$ or a residence time of approximately 5 years). Rapidly decomposable components of fresh litterfall may have residence times of only 0.5 years, whereas the turnover rate (0.0048 $year^{-1}$) of soil organic matter in the tulip poplar forest is equivalent to a turnover time of approximately 200 years. Turnover of carbon through the mortality of woody components of trees (50 g C m^{-2} $year^{-1}$/6990 g C m^{-2} = 0.0071 $year^{-1}$) is equally slow and yields a residence time for carbon in this ecosystem component of nearly 140 years. Overall mean residence time for carbon in the tulip poplar forest was 15 years (1465 g C m^{-2} $year^{-1}$/21,510 g C m^{-2} = 0.068 $year^{-1}$), calculated from the ratio of R_E to total ecosystem carbon pool. How these individual and collective turnover rates for carbon are affected by seasonal phenomena and how they vary among ecosystems of different type and age are questions that yet need to be answered before we can accurately describe in detail the dynamics of carbon in terrestrial ecosystems.

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SUMMARY AND ENVOI

DANIEL A. LIVINGSTONE
Department of Zoology, Duke University, Durham, North Carolina

The life of a subject can be measured by the turnover time of its ideas, the length of time it takes for half of what is taught to beginning students to become completely worthless. On such a scale the geochemistry of carbon has a half-life of something between 10 and 15 years. A few problems, a datum or two, remain of what I learned about it from Professor Hutchinson 20 years ago, but little else. Cosmology, geophysics, and molecular biology turn over a little faster, but 10 or 15 years is quite respectable and places the biogeochemistry of carbon well up among the livelier branches of science.

The summary speaker at a symposium like this is supposed to function as a high-speed shipwright. He hopes to have delivered to him by the participants in the symposium a sufficient number of sound planks and properly hewn timbers that he can peg together in the last few minutes of the last contributor's talk and present to the audience as a vessel of sorts, a skiff or even a sloop, in which they can sail away on the voyage implied by the envoi of George Woodwell's title for these concluding remarks.

Looking back over the papers delivered here during this symposium, I recall a number of very careful and clear expositions of the elements of the subject; I also recall a number of accurate analyses of carbon systems ranging from microscopic calcite crystals through forests to the atmosphere of the entire earth. There have been valuable and well-balanced reviews of several broad aspects of the carbon cycle and original theoretical and observational studies dealing with them. Looking over this wealth of materials, however, I can see no way of fitting the separate contributions together into an integrated structure. These contributions include some bright and shiny new nails, a few odd strakes and sawn frames, and at least two complete vessels, a Deevey schooner and a Broecker full-rigged ship. If you feel like cruising, you will have to use one of them.

William Reiners suggested that a further office of the giver of concluding remarks was to present society at large with some clues on how to handle the problems of politics, war, peace, poverty, heroin, and birth control. I reject that suggestion out of hand, not on the grounds of being a conservative, which was his defense when someone tried to put him in a similar spot, but on the grounds of being an unreconstructed radical.

So, having abdicated both my scientific and my social responsibility, I would still like to recall a few of what seemed to be the high points of this symposium. The thing I enjoyed most was the graph of data from Mauna Loa showing the change of CO_2 in the atmosphere. For those of you who had read the *SCEP Report* and the *Journal of Geophysical Research* with proper care, the majestically rising seasonal cycles may not have had the same freshness, but they made me feel as if I had just put my finger on the beating, living heart of the world. Those data furnished an intellectual and aesthetic experience that was separate from their practical and scientific importance.

I felt the same way when the men from the National Center for Atmospheric Research met each other coming back from their survey of carbon monoxide and methane in the atmosphere. The cycles fell together in the way a geochemist always hopes things will, with agreement within a factor of 3. As an organism who has to breathe the stuff, I was also reassured by their estimate of the normal flux of carbon monoxide through the atmosphere. Biologists around me in the audience gasped at the great quantities of CO that were involved, but I was immensely pleased to learn that, although our local inputs are unpleasant and locally dangerous, we are not likely to wreck the system with them.

During this symposium I have noticed that some authors seemed to be regretting our lack of argument and discussion. These regrets, if such they are, should be abandoned, for they are no more than a complaint about the basic nature of geochemistry.

In science there is a strong tendency to substitute argument for measurement when measurements are hard to come by. Ecologists trying to compare two things, one of which they cannot measure and the other of which they do not understand, are bound to generate a lot of discussion when they meet. They have no choice. Geochemical measurements are not always easy, but they are possible. When the measurements are inadequate, we all know that they can be improved by good careful work. Geochemical meetings may generate less heat than ecological ones, but it is light, not heat, that we are all after in science.

If I were a productivity merchant or a carbon geochemist myself, I would run some risk of feeling complacent and smug. As I am neither, but only a kind of ichthyologist turned pollen analyst, I can say freely what I believe, that this has been an absolutely splendid meeting. I express my own thanks and also, I am sure, the thanks of all who have participated, to George Woodwell for organizing this symposium and also to the Brookhaven staff who handled the details that made it all possible. They have done so with hard work and good humor and with a personal charm, wit, and hospitality that have made this an extremely pleasant three days all of us will remember for years to come.

[Editors' Note: Following the formal sessions of the Brookhaven symposium, a small group of scientists met under the auspices of the Institute of Ecology to consider three questions with respect to the world carbon cycle. The questions were:

1. What are the basic data on the carbon cycle?
2. How is the carbon cycle altered by human activities?
3. What research would best contribute to improved understanding of the world carbon budget and its implications for man?

Dr. William Reiners of Dartmouth College prepared a summary of these discussions for the Institute of Ecology; it is reproduced here with permission of the institute.—George M. Woodwell and Erene V. Pecan]

APPENDIX

A SUMMARY OF THE WORLD CARBON CYCLE AND RECOMMENDATIONS FOR CRITICAL RESEARCH

WILLIAM A. REINERS
Department of Biological Sciences, Dartmouth College, Hanover, New Hampshire
(in cooperation with participants of the Brookhaven Symposium in Biology No. 24)*

THE CARBON CYCLE

It is useful to conceive of the carbon cycle as a series of pools of carbon interconnected by pathways of flux. The entire system ideally represents a steady state that may adjust to new steady states with changes of geological scale. The diagrammatic model of the carbon cycle in Fig. 1 is simpler than others which are presented in this volume, but the model provides an adequate format for the presentation of data. The carbon cycle is divided into four large pools: the atmosphere, land surfaces, ocean waters, and sediments. Each of these is, in turn, subdivided into constituent pools.

In general, the larger the pool, the slower its rate of turnover. Whereas the extent of control that one pool exerts over the cycle may increase with increasing pool size (e.g., atmosphere, biota, oceans, and sediments), the response time of these pools as buffering agents is approximately the inverse of size. It appears that short-term and localized perturbations in carbon exchange

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*See page 381 for names of participants who contributed to this appendix.

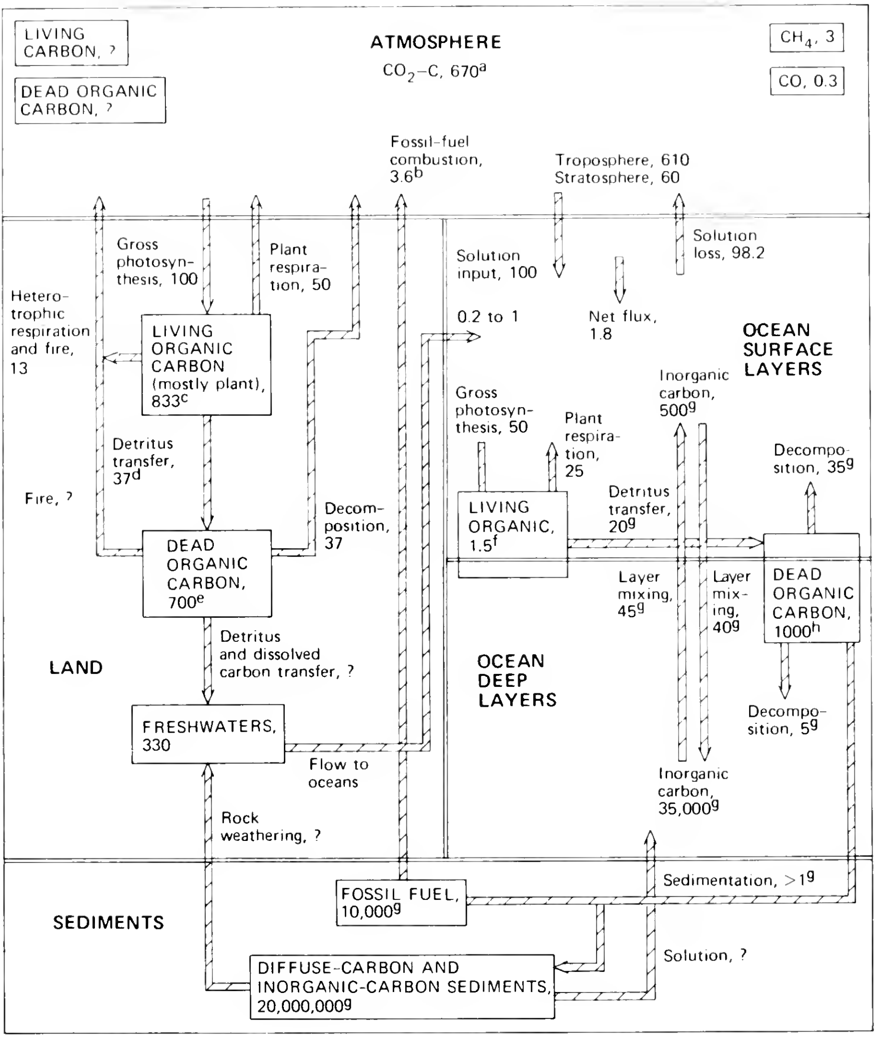

Fig. 1 Diagrammatic model of the global carbon cycle. Estimates are given where possible; sources of these estimates are given below. Question marks indicate that no estimates are available. Figures are all in billions of metric tons of carbon and are derived from estimates of Brookhaven Symposium participants unless otherwise noted. The following are alternative estimates: (a) Other estimates are 683 (SCEP, Ref. 1, page 161) and 700 x 10^9 tons (Bolin).[2] (b) SCEP, Ref. 1, page 304. (c) Bolin[2] estimates 450 x 10^9 tons. (d) Bolin[2] estimates 25 x 10^9 tons (e) Bolin,[2] based on Delwiche's[3] nitrogen estimate and a carbon/nitrogen ratio of 12, an alternative estimate is 9000 x 10^9 tons. (f) Bolin[2] estimates 10 x 10^9 tons. (g) Bolin.[2] (h) Bolin[2] estimates 3000 x 10^9 tons.

are first buffered by the atmosphere and secondarily by land plant biomass together with marine-solution reactions. On the basis of Broecker's report in this volume, marine solution and sedimentation is probably the master control of the cycle in the long term (circa 10^5 years).

Where more than one estimate is given for a pool size or flow rate, the estimate supplied by the Brookhaven group is preferred. Discrepancies in these estimates are testimony to our lack of definitive data on the carbon cycle. It should be of particular interest that these discrepancies seem to be greatest for organic components of the system.

The quality of estimates on the flux rates in Fig. 1 varies widely. In general, rates for physically controlled fluxes and especially atmospheric exchanges are probably the most accurate, and biological rates are the least accurate. Better accuracy is often related to higher levels of homogeneity of process over the earth's surface. There is no analog to mixing to ease the sampling problems of terrestrial processes, such as primary production, forest cutting, or frequency of fire.

It is conceivable that the present carbon cycle may have existed as an overall steady state for periods of time, but known episodes of vulcanism and mountain building plus changes in area of land and sea and changes in climate suggest that the cycle may have shifted repeatedly throughout geological history. The extent of such shifts might be calculated from the geological evidence (see Broecker, this volume). There is little doubt that the steady state is being disturbed in our era, if only due to fossil-fuel combustion. Increases in atmospheric CO_2 are documented in this volume by Ekdahl and Keeling. Accelerated forest cutting, burning, decomposition of soil organic matter, and erosion are likely to be reducing pools of carbon on land. At the same time, eutrophication may be increasing organic pools in fresh and coastal marine waters. Man's activities are undoubtedly increasing rates of rock weathering,[4,5] but we do not know the significance of these perturbations compared with variation in weathering rates throughout the Pleistocene and over the longer term of the Cenozoic with its relatively high orogenic activity.

CRITICAL RESEARCH TOPICS

The net effects of all the influences described in the preceding section are difficult to appraise because inventories and flux rates are poorly known. In many instances processes are insufficiently understood to provide models for predictions. Clearly, estimates of all pools and pathways need refinement, but the Brookhaven group believed that the critical research recommended in this section would yield the most understanding per unit effort.

The Atmosphere

Increases in CO_2

We are fortunate that the best data on the carbon cycle are also the most critical—measurements of the increase in CO_2 content of the atmosphere.

Measurements are available from five sources: Swedish flights,[6] Mauna Loa,[7] the Antarctic,[8] Point Barrow, Alaska,[9] and Upton, N. Y.[10] Of these sources, only Mauna Loa is continuous from 1958 to the present, and it is by far our finest record of CO_2 change on annual and a longer term basis. These data indicate that atmospheric CO_2 has been increasing by 0.2%/year, or 0.7 ppM/year, but that the rate of increase is now about 1.5 ppM/year.

Measurements of the quality of those on Mauna Loa by the Scripps Institution of Oceanography should be expanded on a latitudinal basis. For short-term monitoring, work group 3 of the SCEP Report (Ref. 1, page 195) recommended four stations including Alaska, Hawaii, a South Indian Ocean island, and Antarctica. For effective research purposes, however, they (and the Brookhaven group) recommend 12 such stations, 9 stretched latitudinally across the Pacific, and 3 extended longitudinally, to examine continental effects vs. marine effects on exchange. Such stations would not only monitor increases in atmospheric CO_2, but would provide global estimates of net carbon exchanges by the biota with the seasons. The data would aid in appraising the response of the biota to elevated CO_2 levels.

Further details of this proposal can be found in the SCEP Report (Ref. 1, pages 192 to 198) and in the SMIC Report (Ref. 11, page 244).

The Suess Effect

Prior to the industrial revolution, normally produced ^{14}C was incorporated in living systems at fixed concentrations. With an increase of ^{14}C-poor CO_2 in the atmosphere derived from fossil-fuel combustion, the ^{14}C content decreased proportionately. This dilution of ^{14}C by fossil-fuel injection is termed the "Suess effect" and is a natural means of extending direct measurements of atmospheric CO_2 increase for periods preceding nuclear testing. With testing, ^{14}C production increased above the natural rate and ^{14}C content of plants increased proportionally.

The Brookhaven group strongly urged that tree rings of carefully selected trees from around the world be analyzed for the Suess effect by a single laboratory with a single method and standard. A coordinated effort over several laboratories is needed to resolve questions on the period 1850 to 1950 (compare Bacastow and Keeling, this volume). With these data, we will have a firmer grasp on pre-1950 changes in the atmosphere.

Trace Gases

There are a number of atmospheric trace gases, such as H_2, CH_4, CO, and N_2O, whose production is partly or predominantly biotic (Refs. 12 and 13). Their concentrations are normally low, between 0.1 and 1.5 ppM, so that they have little influence on the tropospheric energy budget. However, their atmospheric lifetimes are long enough that they are mixed in considerable amounts into the stratosphere. There they may be of importance because they and their reaction products interact with ozone, which is important in shielding the earth's surface from the sun's ultraviolet radiation. Higher concentrations of these gases may tend to lower stratospheric ozone concentrations. Such human activities as concentrated cattle feeding and eutrophication of large water bodies may raise these concentrations significantly. It seems conceivable, therefore, that even without large numbers of high-flying supersonic aircraft, man may be affecting stratospheric ozone levels. More insight into the natural cycle of CH_4 and the trace gases is required.

Monitoring

It is possible to monitor some of the trace gases on a worldwide basis by satellite. There are programs under way to test the feasibility of measuring O_3, CH_4, CO, and N_2O. A particularly exciting possibility would be to obtain the global distribution of CO_2 with sufficient precision to allow development of horizontal flux and global balance equations which in turn would allow us to obtain a more accurate estimate of global biological activity. A feasibility study of satellite surveillance was strongly recommended by the Brookhaven group. See Refs. 14 and 15 for further discussion of this topic.

The Ocean

The ocean is unquestionably the largest pool for carbon and therefore an important sink for excess atmospheric CO_2. Because of its importance and because of the complexity of the chemistry of the oceans, no program of research on the global carbon cycle should be attempted without the aid of marine geochemists. Unfortunately material for this report was prepared without the benefit of direct consultation with such a person, and the following treatment on oceans is developed almost entirely from Broecker, Li, and Peng[16] and Broecker's presentation at the Brookhaven Symposium.

The Surface Layer

The surface layer of the ocean is relatively warm and well mixed to a depth of about 70 m and overlies a deep layer of lower temperature. A thermocline of about 1000 m thickness lies between these layers and acts as a barrier to mixing. About 10% of the ocean's surface area does not have an upper, warm layer, so that the atmosphere is in direct contact with the deep layer in these "outcrop" regions.

The CO_2 gas exchange between the surface layer and the atmosphere is related to the partial pressure of CO_2 of the atmosphere and the concentration of dissolved inorganic carbon in the ocean. Concentration of dissolved carbon is related, in turn, to equilibria with bicarbonate and borate ions. Broecker et al.[16] calculated that the oceanic surface layer contained about as much carbon as the atmosphere and that, with an increase in atmospheric CO_2, the surface layer itself would take up only about one-tenth of the increase. Thus transfer to the deep sea is an important limiting process for distribution of excess carbon. Broecker et al.[16] also calculated that the surface layer comes to relatively rapid equilibration with the atmosphere, indicating that it is not an important rate-limiting barrier to movement of atmospheric CO_2 into deep water. The expanding coverage of petroleum films on the ocean surface may become of increasing significance in this respect.

The Deep Layer

Carbon from the shallow layer mixes with deep water through advection, diffusion, and sinking remains of the biota. Deep-water outcrops and advective processes make calculation of mixing an extremely complex process. The technique of measuring $^{14}C/^{12}C$ isotopic ratios is especially complicated by outcrop exposure to the atmosphere and the poor understanding that exists on exchange in these outcrops. Broecker et al.[16] calculated that, as fossil fuels are burned, the percentage distribution of excess carbon will remain the same as at present in the order of 50 to 67% in the atmosphere, 5 to 7% in the warm ocean layer, 23 to 28% in the thermocline, and 0 to 20% in the deep ocean.

Sedimentation

As the acidity of the ocean rises from increased CO_2 solution, sedimented $CaCO_3$ will begin to dissolve. The conversion of $CaCO_3$ to Ca^{2+} and $2HCO_3^-$ through acid solution effectively doubles the capacity for dissolved CO_2. Carbonate solubility appears to be a complex function of temperature, salinity, ← ±pH and pressure and does not increase linearly with depth. Instead, there is a distinct boundary, termed the "lysocline," above which carbonate precipitation predominates and below which carbonate dissolution predominates. The depth of this lysocline can rise or fall as a function of dissolved CO_2 and other factors and thus act as a negative-feedback-control mechanism. According to Broecker et al.,[16] there is sufficient $CaCO_3$ in the upper centimeter of marine sediment to neutralize all the excess CO_2 already produced by man. Therefore carbonate sediments represent an enormous pool that can buffer CO_2 changes in the atmosphere.

The kinetics of this buffering capacity are poorly understood. Some of the uncertainties were discussed by Broecker et al.[16]

> Considerably smaller amounts of CO_2 are needed to bring deeper waters to undersaturation. However, considerably smaller amounts of CO_2 have been made available at these depths. The question as to whether solution will commence first in the deep sea or in the surface water thus involves a detailed knowledge as to how CO_2 penetrates into the sea. As we are not currently in a position to do any more than guess, this question is best left undiscussed.
>
> Another problem that arises is how fast the neutralization will proceed once undersaturation is achieved at any given depth. Very little is known regarding the rates of solution of calcium carbonate in seawater. The problem is further

> complicated by the fact that the carbonate which will undergo solution is generally surrounded by a matrix of silicate detritus. If we are to make long-range predictions, these kinetic questions must be studied.

In summary, Broecker et al.[16] estimate that the sea will continue to remove about 40% of excess carbon and that, within 200 years, marine acidity will reach the point at which $CaCO_3$ sediments will begin to dissolve. At that time the sea will be able to take up even larger amounts of CO_2. Thus the ocean will ultimately absorb enormous amounts of excess CO_2, but the kinetics are slow, and, in the shorter run of the order of 100 years, the atmosphere will hold about 60% of excess CO_2 produced, and we must address ourselves to the climatic and biological consequences of such a change.

Clearly, there are many vital questions to be investigated in the marine geochemistry of carbon. Perhaps the two broad areas requiring the most attention are investigations of ocean mixing, particularly of carbon (compare Stuiver, and Bacastow and Keeling, this volume), and elucidation of the kinetics and controlling factors for dissolved CO_2 interaction with sediments (compare Broecker, Cooke, this volume). In addition, considerable insight on the relation of geotectonic plate movement to the lysoclinal boundary, and the long-term stability of oceanic carbon dynamics can be gained by careful analysis of oxygen and carbon isotope ratios in the sediments as explained by Broecker.

Primary Production and Organic Sedimentation

Eutrophication may be enhancing phytoplankton growth in certain areas. The extent of increased primary production in coastal waters is not known. It is important to know the amount of organic matter that is sedimented. This question is discussed briefly in the papers by Stuiver, and Woodwell, Rich, and Hall.

The Biosphere

Probably the largest single question involving the biosphere and the carbon cycle concerns the extent to which the biota and detritus are acting as sinks for excess atmospheric carbon. As shown in Fig. 1, 3.6×10^9 tons of carbon are currently added to the atmosphere each year. Yet atmospheric content is increasing by 0.7 to 1.5 ppM per year, or 1.8 to 3.6×10^9 tons. About half the injected carbon is going into the oceans or the biota or both. Estimates on the rate of carbon movement into the oceans based on ^{14}C gradients were presented in several papers of the Brookhaven Symposium. These estimates indicated that the biotic pool must be increasing in size (e.g., Bacastow and Keeling, this volume). Whittaker and Likens, on the other hand, contend that biotic mass is decreasing, not increasing, and that these decreases are due to man's activities, principally through conversion of forest land to agriculture, decreases in productivity, and general environmental toxification. Reiners supports the latter view and adds that terrestrial detritus pools are probably shrinking as well through decreases of input and increases in decay rate. Thus, either the estimates of the flux of carbon through the biota, or of the rate of solution into the ocean are in error. This raises a variety of questions, some of which are outlined below. Most of the questions are related to terrestrial ecosystems since these systems account for about two-thirds of the world's net primary productivity and more than 99% of the world's biomass (Whittaker and Likens, this volume).

Photosynthetic Responses to CO_2 Enrichment

There is abundant evidence that enhanced CO_2 concentrations stimulate higher photosynthetic rates under conditions of nonlimiting light, water, and nutrients. The important questions here are: (1) How much stimulation of net annual ecosystem production can be expected, and (2) does increased photosynthesis automatically lead to higher biomass, and thus larger carbon pool sizes?

First, it is not at all clear how much increased primary production can be expected over the earth's surface with CO_2 enrichment. Many vegetation types are limited by other factors for large portions of the time. For example, a 10% increase in CO_2 might lead to a 10% increase in net photosynthesis under ideal conditions, but factors other than CO_2 might be limiting for 75% of the growing season. Thus annual yields of net production might increase by only 25 × 0.10, or 2.5%.

A second point concerns ecosystems dominated by nonwoody plants or small woody plants with characteristically high rates of biomass turnover and prominent grazing pathways of energy flow. Perhaps the best examples of such situations are agricultural lands: as more biomass is produced, more is consumed, and no net gain in carbon storage is possible.

Third, we have the case of ecosystems dominated by woody plants of indeterminant growth form, such as forests. Actually there are limits to sizes of all plants, although it is not always clear whether they are set by genetically controlled senescence or by site factors. Assuming forest productivity is enhanced by increased CO_2 levels, and assuming this extra increment of production is largely stored in biomass or in larger standing states of detritus, again there must be some limit to the biomass and detritus increases. If not set by genetic limits, the increases will be set by some other environmental factor. If some new maximum biomass level is attained, then there will be a new limit to carbon storage. If true, then the land plant biomass could, at best, act as a net carbon sink for only a few decades. This effect would occur mainly in forests, and, to the extent that forests are harvested, the effect would be limited. This result is demonstrated in a simulation of forest growth by Botkin in this volume.

Broecker, Li, and Peng[16] concluded that the biota is probably not an important sink for excess carbon. Their conclusion, however, was based on much lower estimates of living and dead organics (detritus) than those used in this paper and on a rather long estimate of soil-organic-matter turnover time. Their assumption that increased photosynthesis would lead to increased biomass requires critical investigation.

Several research suggestions regarding the influence of elevated CO_2 levels on photosynthesis are raised in the foregoing analysis. Some of these are listed below:

1. Plant responses to increased CO_2 levels should be determined over ranges and combinations of environmentally limiting conditions, such as temperature, moisture, cloudiness, and atmospheric turbidity as they occur at present and as they may accompany climatic changes with increases in CO_2 content.

2. Field studies should be conducted on the ultimate state of ecosystems dominated by nonwoody plants, with and without grazing, under elevated CO_2 stimulation.

3. Determinations should be made of limiting factors for major ecosystems of the world on a time budget followed by an estimation of the fraction of time in which elevated CO_2 might be stimulating.

4. Simulation studies should be initiated to predict the amount of additional CO_2 that would be fixed at increased levels of CO_2 by terrestrial photosynthetic plants, especially by forest plants. Included in these simulations should be the response of plants to CO_2 concentration, the relative global population of the plants involved, and the expected climate (temperature, moisture conditions, cloudiness, atmospheric turbidity, and pollutants). The simulations should integrate the effects of all aspects of microclimate, especially light absorption on a community scale, in addition to the effects of large-scale climate factors. At least one such comprehensive computer simulation has been devised to accurately predict the CO_2 fixation by a monoculture.[17] This type of simulator should be expanded to include mixed population systems with different photosynthetic functions and stand architecture. Eventually it should be joined to a large-scale climate model to give global predictions of CO_2 uptake as affected by CO_2 concentration increase and any concomitant climate changes. Once CO_2 uptake rates are understood, or at least predictable, then more reasonable estimates of biomass accumulation of carbon can be made.

Environmental Toxification

Although increased levels of atmospheric CO_2 may enhance primary productivity, other factors may act to decrease it. Such effluents as smog[18,19] and smelter fumes[20] appear to have mainly local effects; others, such as SO_2 and NO_x compounds may be of wide-scale significance. Indications are that precipitation over the northeastern United States has become increasingly acid over the past 20 years as increased quantities of SO_2 and NO_x are oxidized and hydrolyzed in the atmosphere.[21-23] Recent studies (R. H. Whittaker, in preparation; Bormann, personal communication) strongly suggest that forest growth over much of northern New England has declined since 1950, possibly as a result of this increased acidity.

To appraise regional or global effects of man's activities requires knowledge of the specific effects of toxic compounds. Studies of such effects by smog and heavy metals are under way at present. The acidification of rain over the northeastern United States may present a particularly appropriate opportunity to document the extent of toxification on a regional basis.

Detritus Pools

As shown in Fig. 1, both marine and terrestrial detritus pools are in the same size range as terrestrial biomass. Although these pools appear to be relatively easy to measure, estimates are probably not as good as those for biomass. Some fraction of detritus is relatively labile, with a range of turnover time of minutes to decades, while the rest is relatively refractory, turning over in periods of decades to centuries (see Riley, this volume). In terrestrial systems this latter fraction usually consists of amorphous, altered organic material referred to as humus by soil scientists. Humus is an extremely valuable resource which imparts much of the water and nutrient-holding capacities of soils and is very influential in maintaining beneficial physical soil conditions. Stress will be placed, therefore, on the role of humus in the carbon cycle; but it should be emphasized that net losses of humus through land-management practices can generally be regarded as permanent losses to the productivity of terrestrial ecosystems.

The Work Group on Ecological Effects that contributed to the SCEP Report[1] and other investigators reporting in this volume found it desirable to divide organic carbon into short and long residence times in making a model for the carbon cycle. Short-lived material includes leaves, litter, short-lived animals, and most algae, while long-lived material includes wood, large roots, upper soil humus, and dead organic matter in the oceans. Tables 1 and 2 are from Tables 2.A.1 and 2.A.2 of the SCEP Report;[1] note the first footnote of Table 1 which states that resistant humus and other material have been omitted. Probably a large part of organic carbon has thus been deleted, but it is impossible to tell how much from the brief description in the SCEP Report.

Terrestrial detritus is conveniently concentrated at the soil surface. It is relatively easy to sample and analyze except for humus that requires careful carbon determination. It would be conceptually simple but logistically burdensome to sample detritus pools on a worldwide basis where data are not complete or available. Considerable data are available in the literature, however, and with thoughtful interpretation of such data, much of the world picture could be compiled. One major failing of the literature is inadequate assessment of deep, dispersed humus. The problem is most apparent in some podsols where organic matter in the B horizon, which has largely been ignored, can be greater than all the organic matter in the A horizon. With these precautions, it would be relatively simple to produce a reasonable estimate of current pool sizes with a well-directed program combining field sampling and literature review.

Perhaps to a larger degree than for living biomass, it is convenient to view detritus as a mixed pool where steady-state levels are controlled by a balance of

TABLE 1

ORGANIC CARBON AND ITS RATES OF PRODUCTION*
(Living and Dead, Excluding Incipient Fossil Deposits)

	Area,† 10^6 km^2	Organic carbon pool,† 10^9 metric tons	Production per year,† 10^9 metric tons
Reservoir			
Forest and woodland	48	1012	36
Grassland and tundra	38	314	9
Desert and semidesert	32	59	3
Wetlands	2	30	2
Glaciers and barren	15	0	0
Agricultural	15	165	6
Total terrestrial	150	1580	56
Oceanic	361	703	22
Burning fossil fuel (1970)			4
Atmospheric pool		683	

*Resistant humus and other material with decay rates of 0.001 per year or less have been omitted. Production is "net primary production," i.e., production from photosynthesis minus plant respiration; it represents the yield to animals and decomposers.

†The numbers shown here are intermediate values from the several sources listed in the text. Although these sources present similar estimates, their combined accuracy is not regarded as high; procedures for obtaining global estimates for characteristics of vegetation are still primitive.

inputs and outputs. Inputs are controlled by the quantity of primary production reaching the detritus pools; outputs are basically controlled by decay rates together with pool size.

A series of estimates for inputs into terrestrial detritus pools is presented by Reiners in this volume. These estimates are probably reasonable for many types of more-or-less undisturbed systems. Certain types are poorly represented, however. These are dry or monsoon tropical forests; temperate and tropical savannas; dry, grazed grasslands; various types of arctic tundra; and extreme deserts. Field data would be very useful for these types. Further information of this sort should be forthcoming from the International Biological Programme. Estimates of input are also needed for agricultural systems of the world, together with an analysis of diversion, and rate of change of diversion, of detritus inputs by such human-related activities as forest ground fires, intense grazing, and forestry practice.

Normal decay rates can be determined in apparently steady-state systems by assuming they equal inputs. These rates can be used as reference points for

TABLE 2

SUBDIVISION OF ORGANIC CARBON INTO MATERIALS WITH SHORT OR LONG RESIDENCE TIMES

	Organic carbon pool		Mean residence time, years*	
	Short	Long	Short	Long
Reservoir				
Forest and woodland	62	950	3.1	59
Grassland and tundra	11	303	2.6	63
Desert and semidesert	4	55	2.2	39
Wetlands	1	29	1	36
Agricultural	4	161	1	80
Total terrestrial	82	1498	2.3	62
Oceanic	2	701	0.1	701

*Mean residence of carbon in the atmosphere: 8.8 years. Note: The numbers shown here are not data but intelligent guesses of the way the estimates from Table 1 can be subdivided. Definitions of "short" and "long" residence times are given in the text.

comparison with estimates of change in decay rates perpetrated by man. Man-caused changes in decay rates are generally in a positive direction and are effected through drainage, tilling, fertilization, burning, and erosion. Because of their variation in type and intensity in space, it will be extremely difficult to produce worldwide net estimates, not to mention the difficulties in measurement itself. Nevertheless, a thorough examination of many fields of literature would produce more information on the subject than we now have—which is virtually none—and the most useful field operations would undoubtedly become plainer as such a review and analysis proceeded.

Influences of Land Use on Biomass

The lack of certainty of man's effects on biomass was a major source of discussion at the Brookhaven Symposium. Whittaker and Likens and several others felt that forest harvesting at frequent intervals, conversion of forests to agriculture, and general toxification of environment must all be causing an accelerating decrease in world biomass and thus a decrease in the size of the pool. Others maintained that the effect of forest harvesting results in increased rates of carbon uptake through higher rates of biomass accumulation, thus mitigating higher CO_2 levels in the atmosphere. This dichotomy presents a challenge to a true evaluation of man's impact on the biota. If, indeed, biomass is declining, the rate at which it is declining should be of vital concern.

One approach to such an estimation would be through a coordination of geographic techniques and data on land "development" in the world. Data for the tropics seem especially important. An example of such an estimation is given in Table 2.2 of the SCEP Report.[1] The addition of aerial or satellite surveillance techniques would permit estimates of biomass and, perhaps, production at relatively low cost. For example, satellite photography could provide data on conversion of Asian steppes to wheatlands, taiga to rye, tropical rain forests to croplands, farm and forest land to asphalt, concrete, and shingle.

Modeling

Modeling provides our best means of making predictions for changes in such complex systems as the carbon cycle. In addition, it provides a theoretical base from which investigative research can be planned. A continuous effort, incorporating new data and concepts as they are developed, might best be accomplished with a small team of modelers organized so that optimum information exchange is maintained between modelers and field and literature investigators.

SCEP Recommendations

Many of the contributors to the SCEP Report[1] are also some of the foremost investigators of aspects of the carbon cycle. It is no accident, therefore, that many of the SCEP Report recommendations for action and research are pertinent to a summary of recommended research.

SUMMARY OF RECOMMENDATIONS

Coordinated research on the carbon cycle can be organized in a number of different ways and on a number of scales. One minimal approach would be to sponsor a series of task-force meetings to culminate in such a final interdisciplinary meeting as the Brookhaven Symposium.

Another minimal approach might be the sponsorship of a number of investigators to assemble field data in the literature. These survey reports could be combined with the above-mentioned meeting schedule, together with a modest modeling effort.

A third approach would be to sponsor a pioneering effort combining untested technology with a multidisciplinary investigation of global processes. Perhaps the most promising project of this sort would be the development of a satellite surveillance program to include estimates of trace gases in the atmosphere, CO_2 in the troposphere, land-use changes and biomass estimates on land surfaces, and productivity and pollution patterns in the oceans. A possible prototype of this kind of program, the Earth Resources Technology Satellite (ERTS), is operative.[24]

A fourth approach would be the sponsorship of a specific sector of problems identified for the carbon cycle. In identifying such a sector. the Institute of Ecology would assess its potential for research clientele and make decisions regarding the feasibility and importance of various research problems. If the Institute of Ecology is principally concerned with biological aspects of the carbon cycle, a focus on the question of whether or not world biomass is expanding or contracting and, in either case, the rate at which this is occurring may be of primary concern. On the other hand, the kind of reasoning Broecker et al.[16] (1971) applied to this question might strip it of its importance with regard to the problem of CO_2 increase in the atmosphere. The biological production of trace gases might appear to be more fruitful for the effort involved. Considerable study and discussion by authorities in the various fields represented in this report should be required in order to make a reasonable decision on the application of research effort.

PARTICIPANTS IN THE PREPARATION OF THIS SUMMARY

Allen, Leon H., Jr., U. S. Department of Agriculture, Cornell University, Ithaca, N. Y.
Bacastow, Robert, University of California, San Diego, La Jolla, Calif.
Ehhalt, Dieter H., National Center for Atmospheric Research, Boulder, Colo.
Ekdahl, Carl S., Jr., University of California, San Diego, La Jolla, Calif.
Likens, Gene, Cornell University, Ithaca, N. Y.
Livingstone, Daniel A., Duke University, Durham, N. C.
Olson, Jerry S., Oak Ridge National Laboratory, Oak Ridge, Tenn.
Reiners, William A., Dartmouth College, Hanover, N. H.
Woodwell, George M., Brookhaven National Laboratory, Upton, N. Y.

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LIST OF PARTICIPANTS

ALLEN, LEON H., JR.
U. S. Department of Agriculture
Cornell University
Ithaca, New York 14850

BACASTOW, ROBERT
Scripps Institution of Oceanography
University of California, San Diego
P. O. Box 109
La Jolla, California 92307

BARGHOORN, ELSO S.
Department of Biology
Harvard University
Cambridge, Massachusetts 02138

BAYLEY, SUZANNE E.
University of Florida
Gainesville, Florida 32601

BAYLOR, EDWARD R.
Marine Sciences Research Center
State University of New York
Stony Brook, New York 11790

BAZZAZ, FAKHRI A.
Botany Department
University of Illinois
Urbana, Illinois 61801

BERECH, JOHN J., JR.
Biology Department
Queens College
Flushing, New York 11367

BOTKIN, DANIEL B.
Greeley Memorial Laboratory
Yale University
New Haven, Connecticut 06511

BOUGHEY, A. S.
School of Biological Sciences
University of California
Irvine, California 92644

BROCKELMAN, WARREN Y.
Department of Biology
New York University
University Heights
Bronx, New York 10453

BROECKER, WALLACE S.
Lamont–Doherty Geological Observatory
of Columbia University
Palisades, New York 10964

BURGE, ROBERT E., JR.
Suffolk County Community College
533 College Road
Selden, New York 11784

BURNS, LAWRENCE A.
Environmental Protection Agency
South Florida Ecological Study
Naples, Florida 33940

CADLE, RICHARD D.
National Center for Atmospheric Research
P. O. Box 1470
Boulder, Colorado 80302

CAPLAN, RONALD
Marine Sciences Research Center
State University of New York
Stony Brook, New York 11790

CARLSON, ROGER W.
Forestry School
Yale University
New Haven, Connecticut 06511

CHRISTIANSON, J. D.
Biology Department
Wagner College
Staten Island, New York 10301

CLOUD, PRESTON E., JR.
Department of Geological Sciences
University of California
Santa Barbara, California 93106

COLINVAUX, LLEWELLYA HILLIS
British Museum (Natural History)
11 Rutland Mews East
London, S. W. 7, England

COLINVAUX, PAUL A.
Department of Oceanography
University of Washington
Seattle, Washington 98105

COOKE, ROBERT C.
Institute of Oceanography
Dalhousie University
Halifax, Nova Scotia, Canada

DAMALAS, ANDY P.
Center for Environmental Studies
Division of Forestry and Wildlife Sciences
Virginia Polytechnic Institute
Blacksburg, Virginia 24061

DAMMAN, A. W. H.
Life Sciences Building, U-43
University of Connecticut
Storrs, Connecticut 06268

DAVIS, JOHN D.
Normandeau Associates, Inc.
26 Norfolk Avenue
Northampton, Massachusetts 01060

DEEVEY, EDWARD S., JR.
Florida State Museum
University of Florida
Gainesville, Florida 32601

DINDAL, DANIEL L.
Department of Forest Zoology
State University College of Forestry
Syracuse, New York 13210

DINGER, BLAINE E.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

EDWARDS, NELSON T.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

EHHALT, DIETER H.
National Center for Atmospheric Research
P. O. Box 1470
Boulder, Colorado 80302

EKDAHL, CARL A., JR.
Scripps Institution of Oceanography
University of California, San Diego
P. O. Box 109
La Jolla, California 92037

GASITH, AVITAL
Laboratory of Limnology
University of Wisconsin
Madison, Wisconsin 53706

GOODWIN, M. H.
Department of Zoology
University of Toronto
Toronto 5, Ontario, Canada

GOULDEN, ANNE M.
Editorial Branch
Technical Information Center
U. S. Atomic Energy Commission
Oak Ridge, Tennessee 37830

HARGRAVE, BARRY T.
Marine Ecology Laboratory
Bedford Institute
Dartmouth, Nova Scotia, Canada

HARRIS, W. F.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

HASELBAUER, EDWIN A.
696 Smithtown Avenue
Bohemia, New York 11716

HITCHCOCK, DIAN R.
Norton Lane
Farmington, Connecticut 06032

HOLDSHIP, STEPHEN A.
Department of Zoology
Duke University
Durham, North Carolina 27706

JANAK, JAMES F.
Watson Research Center
IBM Research
Yorktown Heights, New York
10598

JORDAN, CARL F.
Radiological Physics Division
Argonne National Laboratory
Argonne, Illinois 60439

KAPLAN, WARREN
Marine Biological Laboratory
Woods Hole, Massachusetts 02540

KEELING, CHARLES D.
Scripps Institution of Oceanography
University of California, San Diego
P. O. Box 109
La Jolla, California 92307

KEEN, ROBERT
Department of Zoology
University of Vermont
Burlington, Vermont 05401

KELLOGG, WILLIAM W.
National Center for Atmospheric Research

P. O. Box 1470
Boulder, Colorado 80302

KILHAM, PETER
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

KILHAM, SUSAN S.
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts 02543

LEO, RICHARD F.
Biological Laboratories
Harvard University
Cambridge, Massachusetts 02138

LI, YUAN-HUI
Hoffman Laboratories
Harvard University
Cambridge, Massachusetts 02138

LIKENS, GENE
Ecology and Systematics
Cornell University
Ithaca, New York 14850

LIVINGSTONE, DANIEL A.
Zoology Department
Duke University
Durham, North Carolina 27706

LOUCKS, ORIE L.
Department of Botany
University of Wisconsin
Madison, Wisconsin 53705

MACHTA, LESTER
National Oceanic and Atmospheric
Administration
8060 13th Street
Silver Spring, Maryland 20910

MELACK, JOHN M.
Zoology Department
Duke University
Durham, North Carolina 27706

MICHAEL, HENRY N.
Radiocarbon Laboratory
Museum Applied Science Center for
Archaeology
University of Pennsylvania
Philadelphia, Pennsylvania 19104

MITCHELL, J. MURRAY, JR.
Environmental Data Service
National Oceanic and Atmospheric
Administration
Silver Spring, Maryland 20910

MOORE, ALLEN
Department of Biology
Western Carolina University
Cullowhee, North Carolina 28723

OLSON, JERRY S.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37831

PARKER, RICHARD A.
Department of Zoology
Washington State University
Pullman, Washington 99163

RABSON, ROBERT
Biology Branch
Division of Biomedical and Environmental
Research
U. S. Atomic Energy Commission
Washington, D. C. 20545

RALPH, ELIZABETH K.
Radiocarbon Laboratory
Museum Applied Science Center for
Archaeology
University of Pennsylvania
Philadelphia, Pennsylvania 19104

REICHLE, DAVID E.
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

REINERS, WILLIAM A.
Department of Biological Sciences
Dartmouth College
Hanover, New Hampshire 03755

RICHARDSON, JONATHAN L.
Biology Department
Franklin and Marshall College
Lancaster, Pennsylvania 17604

RILEY, GORDON A.
Institute of Oceanography
Dalhousie University
Halifax, Nova Scotia, Canada

ROSENBERG, NORMAN J.
Department of Horticulture and Forestry
University of Nebraska
Lincoln, Nebraska 68503

SILVA, CARLOS C. A. E.
University of São Paulo
São Paulo, Brazil

SOLLINS, PHILLIP
Environmental Sciences Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee 37830

SPACIE, ANN
Tarrytown Technical Center
Union Carbide Corporation
Old Saw Mill River Road
Tarrytown, New York 10591

STEARNS, FOREST
Botany Department
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

STEVENS, CHARLES M.
Argonne National Laboratory
Argonne, Illinois 60439

STUIVER, MINZE
Department of Geology and Zoology
University of Washington
Seattle, Washington 98195

SUESS, HANS E.
Department of Chemistry
University of California, San Diego
La Jolla, California 92037

TELEGADAS, KOSTA
Air Resources Laboratory
National Oceanic and Atmospheric Administration
Silver Spring, Maryland 20910

TRAMA, FRANCESCO B.
Department of Zoology
Rutgers University
New Brunswick, New Jersey 08903

VADAS, ROBERT L.
Departments of Oceanography and Zoology
University of Maine
Orono, Maine 04473

VITOUSEK, HELEN
Department of Biological Sciences
Dartmouth College
Hanover, New Hampshire 03755

VITOUSEK, PETER
Department of Biological Sciences
Dartmouth College
Hanover, New Hampshire 03755

WALLACE, ROBERT L.
Dartmouth College
Hanover, New Hampshire 03755

WALLIS, JAMES R.
Watson Research Center
IBM Research
Yorktown Heights, New York 10598

WELCH, REYNOLD S.
Biology Department
Suffolk County Community College
Selden, New York 11784

WETZEL, ROBERT G.
W. K. Kellogg Biological Station
Michigan State University
Hickory Corners, Michigan 49060

WHITFORD, PHILIP B.
Botany Department
University of Wisconsin-Milwaukee
Milwaukee, Wisconsin 53201

WHITTAKER, ROBERT H.
Ecology and Systematics
Cornell University
Ithaca, New York 14850

WRIGHT, ROBERT D.
Department of Biology
University of Redlands
Redlands, California 92373

PARTICIPANTS FROM BROOKHAVEN NATIONAL LABORATORY

ANDERSON, R. CHRISTIAN
BALLARD, JOHN T.
BOND, VICTOR P.
BORES, ROBERT J.
BOTTINO, PAUL J.
CARLSON, PETER S.
CHRISTMAN, DAVID R.
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GREENHOUSE, NATHANIEL A.
GRIST, ELEANOR
GRIST, KENNETH L.
HALL, CHARLES A. S.
HALL, MARY C.
HILL, FRANK B.
HOLT, BUFORD R.
HON, PING-KAY
HORN, FREDRICK T.
HOUGHTON, RICHARD A.
JAHN, ALEXANDRA
KLEIN, J. RAYMOND
KLUG, ERIC E.
KONDRATUK, HELEN Z.
LACKS, SANFORD A.
LEDBETTER, MYRON C.
MEYER, DOROTHY P.
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MUCKERMAN, JAMES F.
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OLSON, JOHN M.
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RUDERT, MARJORIE L.
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SHOTKIN, LOUIS M.
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WILLIAMS, RICHARD D.
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WYSOCKI, JEANNE R.

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